U.S. DEPARTMENT OF ENERGY

SUBSURFACE BIOGEOCHEMICAL RESEARCH AND TERRESTRIAL ECOSYSTEM SCIENCE JOINT INVESTIGATORS MEETING

POTOMAC, MARYLAND

MAY 14-15, 2013

The Subsurface Biogeochemical Research and Terrestrial Ecosystem Science programs within the Department of Energy's Office of Biological and Environmental Research (BER) held their first annual joint investigators meeting May 14-15, 2013, in Potomac, Maryland, just north of Washington, D.C. Funded projects provided abstracts and posters summarizing their progress to date.

Office of Science
Office of Biological and Environmental Research
http://science.energy.gov/ber/

Subsurface Biogeochemical Research Program
http://doesbr.org/
Program Managers
Paul Bayer: paul.bayer@science.doe.gov
David Lesmes: david.lesmes@science.doe.gov

Terrestrial Ecosystem Science Program
http://tes.science.energy.gov/
Program Managers
J. Michael Kuperberg: Michael.Kuperberg@science.doe.gov
Daniel Stover: daniel.stover@science.doe.gov

Prepared by
Biological and Environmental
Research Information System
Oak Ridge National Laboratory
Oak Ridge, TN 37830
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SUBSURFACE BIOGEOCHEMICAL RESEARCH

ARGONNE NATIONAL LABORATORY (ANL)

NAME: Maxim Boyanov

ORGANIZATION: Argonne National Laboratory

PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Update on the factors controlling U(IV) speciation during (bio)reduction of aqueous and solid-phase U(VI): effects of phosphate and Ti(IV)

ABSTRACT: Uranium is a radionuclide contaminant of significant concern at DOE nuclear material production facilities such as Oak Ridge, TN, Rifle, CO, and Hanford, WA. Reductive remediation approaches, whereby soluble U(VI) is reduced to U(IV), have been studied extensively because of their potential to decrease U concentrations below the drinking water standard (<30 μg/L) through the precipitation of uraninite (UO_2). However, experiments at the Rifle, CO, site show that reduced U(IV) is not present as uraninite in the solid phase (Bargar et al., PNAS 2013, p.4506), and the analysis of reduced sediments from the Oak Ridge field site during the 2009 Emulsified Vegetable Oil (EVO) biostimulation campaign shows that U(VI) is reduced to a non-uraninite U(IV) form (Boyanov et al., in prep.). Despite these observations, the factors controlling the molecular speciation of U(IV) following U(VI) reduction and the stability of non-uraninite U(IV) remain poorly understood. Improved knowledge is essential for advancement of the current predictive models and in the design of nuclear fuel repositories.

As part of understanding uranium transformations and speciation in field-site sediments, we are continuing to study the biological and abiotic reduction of U(VI) in laboratory systems of increasing complexity. Here we show that Ti(IV) impurities inhibit uraninite formation during the abiotic reduction of aqueous U(VI) by magnetite and by other Fe^{II}-containing phases. Ti(IV) is commonly incorporated in natural magnetite and is also found in the magnetic sediment fraction at the Hanford nuclear site. Titanium-doped magnetite of varying Ti content ($Fe_{3-x}Ti_xO_4$, $0<x<0.5$) was reacted with aqueous U(VI). Analysis of the solids by U L_{III} edge XANES and EXAFS spectroscopy indicates that Ti incorporation in magnetite does not affect its ability to reduce U(VI) to U(IV). Reactions with Ti-doped magnetite resulted in a non-uraninite U(IV) phase, whereas reactions with pure magnetite resulted in nanoparticulate uraninite. Analysis of the EXAFS data indicates that the non-uraninite U(IV) is stabilized abiotically by the formation of a previously unobserved corner-sharing complex between Ti and U(IV), with a U(IV)-Ti distance of 3.43 Å.

We are also continuing to study the biomolecular mechanisms of U(VI) reduction by metal-reducing bacteria. Here we show that *Shewanella*, *Anaeromyxobacter*, and *Geobacter* spp. are able to slowly reduce U(VI) added in the form of hydrogen uranyl phosphate solids (HUP). Comparisons between bioreduction experiments that either favored or inhibited HUP dissolution suggest that these bacteria reduce predominantly the dissolved U(VI) fraction, despite their known capabilities to inject electrons into solid-phase Fe(III) oxidants. Analysis of the reduced U(IV) species in the solid-phase indicate the formation of a non-uraninite, edge-sharing U(IV)-phosphate complex, with a U(IV)-P distance of 3.40 Å. A similar form of U(IV) was observed in U(VI) reduction by the field-site isolate *Anaeromyxobacter* strain FRC-R5.

The stabilization of diverse non-uraninite U(IV) species by trace phosphate or Ti(IV) suggests that the U(IV) geochemistry relevant to subsurface systems may be more complex than just the formation of the least soluble form of U(IV), uraninite. Further studies are needed to elucidate the formation/stability of U(IV) species and to obtain the necessary information for their incorporation in computational field-scale models.

NAME: Ken Kemner

ORGANIZATION: Argonne National Laboratory

PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Investigations of the physical and chemical characteristics of carbon in the subsurface and root zones to improve Earth system modeling of the biogeochemical cycling of carbon

ABSTRACT: Advanced mechanistic understanding of carbon (C) biogeochemical cycling is essential for the development of Earth System Models. Critical for development of that mechanistic understanding is the determination of the physical characteristics and chemical speciation of C in subsurface and root zone environments. Hard x-ray microtomographic imaging of soil pore structure in unaltered soil aggregates is a powerful approach to understanding the physical structure of soil and the physical controls of C partitioning within soils (Kemner, et al., 1998). In addition, x-ray spectroscopy- and microscopy-based investigations of the 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 non-resonant inelastic x-ray scattering (NIXS) technique, which enables measurement of C 1s x-ray absorption spectra using high energy x-rays. Applying NIXS at an insertion device beam line at the Advanced Photon Source (APS) enables measurement of these types of samples without the need for containment in vacuum. We are integrating x-ray microtomographic, NIXS, and STXM approaches to develop an advanced mechanistic understanding of C cycling

Our initial NIXS investigations of C speciation in a variety of standards, microbial biomass, and soil constituents from peats, humic materials, and Alaskan permafrost (Mishra, et al., 2013) showed that NIXS measurements can distinguish important C moieties like aromatic-C, amide-C, phenol-C, carbonyl-C, and carboxyl-C. Additionally, we have shown that NIXS can enable quantitative determination of the relative percentage composition of these moieties. Comparisons of results determined with NIXS to those determined with nuclear magnetic resonance (NMR) measurements indicate agreement and complementarity of the two approaches. Integration of soft x-ray STXM approaches (presently being developed at the APS) into these investigations will provide the spatial resolution information that will be complementary to NIXS measurements of bulk samples.

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 the aggregates (Bailey, et al., 2013). X-ray transmission microtomographic measurements showed that a greater proportion of the pore space in the small- and medium-sized macroagregates is present as relatively smaller pores, resulting in greater overall porosity and pore-mineral interface area.

NAME: Edward O'Loughlin
ORGANIZATION: Argonne National Laboratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Coupled Processes in the Biogeochemical Dynamics of Fe, S, and C under Sulfate- and Iron-Reducing Conditions

ABSTRACT: The mobility of contaminants, the availability of C and nutrients, and the geochemical character of groundwater in subsurface environments is closely tied to the biogeochemical cycling of the major elements, particularly the redox cycling of C, Fe, and S. Because these cycles occur concurrently and interdependently, predicting each element's transformations requires a fundamental understanding of the highly coupled biotic and abiotic processes that drive the biogeochemical cycling of C, Fe, and S in subsurface environments.

To better understand the effects of specific electron donors on the biogeochemical dynamics of Fe, S, and C under sulfate- and iron-reducing conditions, we created batch systems containing either acetate, lactate, or glucose as electron donors and ferrihydrite and sulfate as electron acceptors. The batch systems were inoculated with the native microbial community present in sediment from the Rifle, CO, IFRC site. Mineral transformations were monitored by XRD and XAFS spectroscopy, and changes in the microbial communities were determined from 16S rRNA-based tag sequence inventories. All electron donors tested promoted ferrihydrite reduction to varying extents: glucose >> lactate > acetate. The rates and extents of sulfate reduction were faster with lactate than with acetate, while glucose did not stimulate sulfate reduction. Surprisingly, the two replicates of the glucose-amended incubations exhibited different rates and extents of Fe^{II} production and glucose fermentation product profiles. The communities in both of the glucose-amended incubations shifted rapidly and remained stable for the rest of the experiment, consistent with the rapid initial reduction of iron with glucose; however, the microbial populations in each replicate were very different. The incubations with acetate and lactate also showed major community shifts over time, but they were different from each other and from the community profiles in glucose amended incubations.

A parallel set of incubations containing lactate as the electron donor and ferrihydrite, goethite, or lepidocrocite in the presence of high (10 mM) or low (0.2 mM) sulfate was also examined. In the presence of low sulfate, Fe^{III} reduction was slow and limited for all of the Fe^{III} oxides. However, the extent of Fe^{III} reduction increased more than 10 times in the presence of high sulfate. In addition, the extent of Fe^{III} reduction was higher in ferrihydrite and lepidocrocite incubations than in goethite incubations. The concurrence of Fe^{III} and sulfate reduction in the high-sulfate incubations, along with the low levels of Fe^{II} production in the low-sulfate incubations, suggests that Fe^{III} oxide reduction in these systems was primarily the result of abiotic reduction of Fe^{III} by sulfide produced by dissimilatory sulfate-reducing bacteria (DSRB) and not via direct reduction by dissimilatory iron-reducing bacteria (DIRB). Distinctly different community profiles were observed for each of the Fe^{III} oxides. These results suggest that when dissimilatory iron reduction is slow and both sulfate and Fe^{III} oxide are available, sulfide produced by DSRB can drive Fe^{III} oxide reduction. However, the rate and extent of the Fe^{III} reduction by sulfide are strongly affected by the specific Fe^{III} oxide.

We also examined the potential coupling of Fe and S redox processes under alkaline conditions, where the reduction of Fe^{III} by DIRB ceases to be energetically favorable; under these conditions, metal

reducers must utilize alternate electron acceptors. One possible alternative is elemental sulfur (S^0), which is produced when dissolved sulfide (a product of microbial sulfate reduction) reacts with Fe^{III} phases. Using geochemical modeling, we show that unlike the reduction of ferric minerals, the reduction of S^0 becomes more energetically favorable as pH increases. We observed experimentally that, under alkaline conditions, *Shewanella oneidensis* MR-1 is capable of reducing S^0 to sulfide, which then reacts with ferric minerals to form Fe^{II}. These results suggest that in slightly alkaline environments where both sulfate and Fe^{III} are available, metal-reducing bacteria may survive primarily by respiring the S^0 created by DSRB.

SUBSURFACE BIOGEOCHEMICAL RESEARCH

LAWRENCE BERKELEY NATIONAL LABORATORY (LBNL)

NAME: Harry Beller

ORGANIZATION: Lawrence Berkeley National Laboratory

PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Characterizing Metabolic Potential of the Subsurface for SFA 2.0

ABSTRACT: The role of the Metabolic Potential component of the LBNL Scientific Focus Area is to inform the overarching genome-enabled biogeochemical model (GEWaSC) and characterize prevalent metabolic pathways in subsurface microbial communities that mediate carbon and electron flux. The long-term objectives of Metabolic Potential are twofold: (1) Develop a concerted approach involving field and laboratory experiments and state-of-the-art informatics to characterize the metabolic diversity of subsurface microbial communities at the genome scale, integrating metagenomic, etatranscriptomic, metaproteomic, physiological, and geochemical/metabolite data to strengthen and validate models of carbon and electron flux, and (2) As inputs to the GEWaSC model, establish functional guilds that impact the carbon and coupled N, S, and Fe cycles in different subsurface regions. Major scientific objectives/questions to be addressed include the following: (1) Establish how aquifer microbial processes change in response to periodic or long-term geochemical changes and how responses to perturbation vary in biogeochemically distinct regions of the aquifer. Specifically, in what ways do the metabolic lifestyles/pathways of microorganisms modulate in response to seasonal changes in redox conditions as a function of water table fluctuation or organic matter loading? (2) To what extent can we establish the linkages between modes of degradation of organic matter (e.g., modification of specific compounds or functional groups) and the genetically encoded metabolic potential of microbial communities to which it is exposed? and (3) Establish under what conditions chemolithoautotrophy can play a significant role in subsurface carbon and electron flow.

The Metabolic Potential component will integrate multiple lines of investigation to address its key objectives and science questions: (1) state-of-the-art meta-omics analysis, (2) targeted physiological analysis (using high-throughput microplate assays with fluorophore-labeled substrates, as possible), (3) high-throughput microbial isolation, and (4) experimental systems consisting of field studies and laboratory studies (particularly flow-through columns). Meta-omics analysis will constitute the core of the Metabolic Potential component. Metagenome information will elucidate the phylogenetic membership of the community (e.g., using EMIRGE), and, after appropriate binning and genome reconstruction, can allow for highly detailed hypotheses to be developed about the metabolic lifestyles of individual community members (e.g., Wrighton et al. 2012; Handley et al. 2012). In conjunction with detailed, synchronous physicochemical data, metatranscriptome and metaproteomic data will provide information about which genes are most important to the organism under targeted sampling conditions and will be used to validate metabolic predictions. The Metabolic Potential component will take advantage of a JGI Community Sequencing Program (CSP) allocation as well as ggKBase, a product of DOE's KBase program. Field (groundwater and aquifer sediment) samples will include background areas, critical zones (e.g., zones subject to water table fluctuations or naturally bioreduced zones containing high loadings of native organic matter), and samples from perturbation experiments. Planned laboratory column studies will include (1) experiments simulating water table fluctuations, in which formerly anoxic sediments are subjected to dissolved oxygen (in parallel with field perturbation experiments) and (2) detailed studies of microbial metabolism of native Rifle organic matter, involving in-depth meta-omics and organic matter characterization.

Some examples will be given of how prior LBNL SFA and Rifle IFRC genome-enabled studies will provide knowledge and expertise relevant to the proposed work for SFA 2.0.

NAME: Nicholas Bouskill
ORGANIZATION: Lawrence Berkeley National Laboratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Prognosing the niche and activity of microbial functional guilds using trait-based modeling

ABSTRACT: Soil biogeochemistry and microbial ecology are tightly coupled through complex microbial communities that mediate the majority of biogeochemical cycles. The structure and function of these microbial communities are shaped by transient physical, chemical and biological interactions. These communities, in turn, affect an array of environmental parameters (e.g., pH, oxygen concentrations, and nitrogen availability) and shape biogeochemical reaction networks related to organic matter breakdown and nutrient cycling. Feedbacks between systems biogeochemistry and the composition of microbial populations has provoked interest in improving representation within ecosystem models of certain microbial functional guilds (i.e., microbes catalyzing the same reaction independent of phylogeny). Trait-based models are promising tools to represent the multidimensional niche of microbial functional groups with their fitness prescribed by their combined traits and trade-offs. This approach allows prediction of the distribution of distinct functional communities along spatial and temporal gradients. Here we describe the development and testing of a trait-based model of autotrophic microorganisms, in particular we focus on the seldom-studied nitrite-oxidizing bacteria (NOB). The NOB catalyze the conversion of NO_2 to NO_3 and our previous modeling work has shown this group to be important in determining net fluxes of N_2O produced by ammonia-oxidizing organisms. We subsequently mapped the niche of three distinct groups of this functional guild, an oligotrophic autotroph, a copiotrophic autotroph, and a mixotroph, across physicochemical gradients in substrate (nitrite and organic carbon) and oxygen. We will discuss this data here with further reference to the importance of emergent communities in determining the rate of NO_2-oxidation.

Looking forward, trait-based models are ideal frameworks for integrating the kind of information readily available from dvanced omic techniques. We provide examples of how this information can be used to (a) directly inform the value of different traits, and (b) weight the initial parameterization of certain traits (e.g., substrate utilization) to specific groups within a functional guild.

NAME: Mark Conrad
ORGANIZATION: LBNL
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Isotopic Signatures of Groundwater Sources at the Rifle Site

ABSTRACT: The DOE's Old Rifle site is a former uranium mill site situated on a floodplain of the Colorado River in western Colorado. The geology of the site consists of 6-7 m of Quaternary alluvium overlying a relatively impermeable unit of the Tertiary Wasatch Formation. A 2-3m thick perched water aquifer on top of the Wasatch contains elevated concentrations of uranium that are derived from a combination of uranium left from the milling activities and elevated natural uranium in the groundwater. Understanding the importance of the various possible sources of uranium is key to determining realistic remediation goals for the site. To assess the importance of external background sources of uranium, we are conducting a chemical and isotopic study of potential sources of the groundwater at the site.

The Rifle floodplain is bounded on one side by the Colorado River and a combination of eroded units of the Wasatch Formation and terraced Quaternary alluvial deposits around the rest of the floodplain. Additional potential sources of groundwater include surface infiltration. Water derived from the Colorado River is very dilute and contains very low levels of uranium. Surface infiltration is limited by clay-rich sediments from the alluvium used to cover the site following removal of contaminated sediments in the 1990s. These clay-rich units also cover much of the terraced alluvial deposits adjacent to the site, suggesting that infiltration through those sediments is also limited and possibly similar in chemistry to infiltration at the site.

Water samples from seeps and springs emanating from eroded exposures of the Wasatch Formation have the highest dissolved salt concentrations including sulfate concentrations as high as 31.5 mM (compared to <1 mM in the Colorado River and ~2 mM in seeps from the overlying alluvium) with δ^{34}S values as low as -18‰. These high sulfate concentrations and low δ^{34}S values are attributed to dissolution of gypsum veins in the Wasatch with δ^{34}S values as low as -56‰ that were derived from rapid oxidation of localized deposits of reduced organic matter in the Wasatch Formation (Conrad et al., in prep). The high sulfate waters also have uranium concentrations as high as 0.65 µM, which could also be derived from the oxidation of the reduced zones. The maximum uranium concentrations measured in the Rifle groundwater are ~1.5 µM, suggesting that as much as 40% of the uranium in the groundwater is derived from natural sources. Sulfate concentrations in Old Rifle groundwater are also elevated (up to 10 mM) and have low sulfur isotope ratios (δ^{34}S values as low as -10‰). Simple mixing models indicate that 30-40% of the groundwater in the Old Rifle aquifer is derived from Wasatch groundwater. There are small variations in the hydrogen and oxygen isotope compositions of the water at the site, with the two end-members being Colorado River water (average δD = -125‰, δ18O = -16.7‰) and the highest sulfate Wasatch waters (average δD = -107‰, δ18O = -13.4‰). This suggests that the water isotope compositions may represent a conservative tracer for inputs of Wasatch water to groundwater at the site. The ^{87}Sr/^{86}Sr of groundwater, springs and surface covers a wide range (0.7106-0.7112), varying systematically with Sr concentration across the flood plane. Taken together, the isotope signatures provide a promising method for distinguishing natural uranium inputs to the Old Rifle aquifer from uranium derived from the milling activity.

NAME: Jennifer Druhan
ORGANIZATION: LBNL / Stanford University
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Sulfur cycling and isotopic fractionation in biostimulated Rifle sediments

ABSTRACT: Biologically catalyzed redox reactions often produce large stable isotope fractionations between reactant and product species. The isotope ratios of these species contain information complementary but distinct from traditional concentration measurements, and therefore provide novel constraints on the rates, progression and secondary mineralization processes associated with *in situ* biostimulation. Stable isotope ratios of sulfur have been measured over three consecutive years of acetate-enabled biostimulation at the US Department of Energy's Rifle Integrated Field Research Challenge (IFRC) site. The data show a previously undocumented trend towards an earlier onset of sulfate reducing conditions over subsequent amendments, from 20 days in the 2007 experiment to 4 days in the 2009 experiment (Druhan et al., 2012). Such novel insights into the cycling of metals and radionuclides in the near surface environment through the lens of stable isotope distributions motivates a quantitative, mechanistic treatment of stable isotope distributions in a process based reactive transport model. This study demonstrates a mechanistic incorporation of the stable isotopes of sulfur into the CrunchFlow reactive transport code to model the range of microbially-mediated redox processes affecting kinetic isotope fractionation. Previous numerical models of microbially mediated sulfate reduction have suggested that $\delta^{34}S$ fractionation is not accurately simulated when substrate concentrations become limiting because the fractionation factor decreases under these conditions. However, we suggest a single kinetic fractionation factor can be used to accurately simulate $\delta^{34}S$ variation over a wide range of substrate concentrations when the effect of the half saturation constant on the behavior of individual isotopes within Monod or Michaelis-Menten-type rate expressions are appropriately considered. This new model capability is tested through simulation a large-scale column study designed to replicate field scale conditions of an organic carbon (acetate) amended biostimulation experiment in Old Rifle sediments (Druhan et al., 2013). The reactive transport model accurately reproduced the measured enrichment in $\delta^{34}S$ of both the reactant (sulfate) and product (sulfide) species of the reduction reaction using a single fractionation factor of 0.987 obtained independently from field-scale measurements. The model also accurately simulated the accumulation and $\delta^{34}S$ signature of solid phase elemental sulfur over the duration of the experiment, providing a new tool to predict the isotopic signatures associated with reduced mineral pools formed during redox transitions. Extension of the model to the $\delta^{34}S$ data collected during biostimulation experiments at the field site demonstrates that the trend towards an earlier onset of sulfate reduction is a result of shifts in the population size and spatial distribution of sulfate reducing bacteria in response to multiple stimulation events.

Druhan et al. (2012) Timing the onset of sulfate reduction over multiple subsurface acetate amendments by measurement and modeling of sulfur isotope fractionation. ES&T, 46(16), 8895 – 8902.
Druhan et al. (2013) A large column analog experiment of stable isotope variations during reactive transport: I. A comprehensive model of sulfur cycling and $\delta^{34}S$ fractionation. GCA (in review)

NAME: Susan Hubbard
ORGANIZATION: Lawrence Berkeley National Lab
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: LBNL Sustainable Systems Scientific Focus Area: Overview

ABSTRACT: A key gap in our understanding of subsurface processes is the lack of quantification of carbon/nutrient fluxes in the subsurface, including the coupling of vertical and lateral hydrological and biogeochemical fluxes in and across deeper soils, the vadose zone, groundwater, and the hyporheic zone. These coupled fluxes could have significant implications for down-gradient water quality and ecosystem functioning. A second key challenge is quantification of microbial metabolic activity in dynamic subsurface environments. In spite of their critical role, very little is known about the manner in which subsurface microbial communities are organized, the primary determinants of how this organization evolves, and the nature of interactions between the microbes and their physical/chemical environment. New developments in sequencing and post-sequencing bioinformatics and in systems biology have rendered it more feasible to predict how microbial communities will change in response to environmental perturbations. Finally, advanced multiscale simulation capabilities that can predict how information stored in a microbial community metagenome is translated into larger system biogeochemical functioning, and how environmental forcings influence microbial metabolic activity, are entirely missing. New multiscale reactive transport simulation capabilities are needed that couple terrestrial microbial composition, competition, activity, and adaptation to biogeochemical processes and the hydrologic cycle in a manner that honors landscape characteristics, hydrological boundaries, lateral and vertical fluxes, biogeochemical transformations, and subsurface heterogeneity.

The Sustainable Systems Scientific Focus Area 2.0 Science Plan ("SFA 2.0") has been developed to advance predictive understanding of complex and multiscale terrestrial environments relevant to the DOE mission through specifically considering the scientific gaps defined above. The Grand Science Question and Grand Deliverable associated with this SFA 2.0 Science Plan are as follows:

Grand Science Question: How will 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; how will these processes evolve over time; and what effect will these interactions have on overall watershed biogeochemical functioning?

Grand Deliverable: Development of a **G**enome-**E**nabled **Wa**tershed **S**imulation **C**apability (**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 functioning, and how these interactions co-evolve.

Activities associated with the first three-year review period ("Phase I") will be primarily implemented at the Rifle, CO site. The Rifle Site provides favorable hydrogeochemical conditions and foundational understanding, datasets, models, and infrastructure that will enable us to make significant and efficient advances during the first three years of the project. At this site, we will test specific aspects of the grand challenge question and deliverable. Initiating the project at the Rifle Site will allow the SFA to develop critical capabilities and understanding before transitioning to a natural or managed ecosystem site that has additional complexity.

NAME: Peter Nico

ORGANIZATION: Lawrence Berkeley National Laboratory

PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Coupling between iron and organic matter cycling: implications for carbon stability and iron reactivity

ABSTRACT: There is increasing evidence that the fate of Fe and organic matter are intimately linked. However, much of this evidence comes from bulk scale observations from which mechanisms must be inferred. Our work has provided mechanistic insights into the coupling of Fe and OM cycling in very geochemically diverse microenvironments. In one case, precipitation of Fe is used to remove DOM from an agricultural drain. The resulting Fe-OM co-precipitates are shown to be resistant to reductive dissolution and to maintain low solution DOM concentrations. Solution concentrations of Fe and DOM were monitored, floc crystallinity was determined using X-ray diffraction, and the composition and distribution of functional groups was assessed using scanning transmission X-ray microscopy (STXM) and Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. Results indicate co-precipitation of Fe with DOM forms a non-crystalline floc that prevents further Fe crystallization regardless of pH, Fe:DOM ratio, and type of reductant added. There was no evidence that exposure to reducing conditions led to release of DOM from the floc, indicating that co-precipitation with complex natural OM in aquatic environments may stabilize Fe hydroxides against crystallization upon reaction with reduced species and lead to long term sequestration of the DOM. STXM analysis identified spatially distinct regions with remarkable functional group purity, contrary to the model of DOM as relatively uniform complex polymer lacking identifiable organic compounds. Polysaccharide like OM was strongly and directly correlated with the presence of Fe but showed different Fe binding strengths depending on the presence of carboxylic acid functional groups, whereas amide and aromatic functional groups were inversely correlated with Fe content. In a second microenvironment of a fungi-dominated O-horizon of old-growth forest soils thin organic coatings on Fe (hydr)oxides containing soil microstructures are enriched in aliphatic C and amide N, suggesting a concentration of microbial lipids and proteins on these surfaces. A possible explanation for the results of our micro-scale investigation of chemical and spatial patterns is that amide N from chitinous fungal cell walls was assimilated by hyphae-associated bacteria, resynthesized into proteinaceous amide N, and subsequently concentrated onto Fe (hydr)oxide surfaces. These data provide mechanistic support for recent work proposing the importance of roots and fungi in long-term carbon stabilization. Taken together the two studies show the general importance of Fe redox cycling to understanding the fate of OM in natural systems.

NAME: Carl Steefel
ORGANIZATION: Lawrence Berkeley National Laboratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Development of a Genome-Enabled Watershed Simulation Capability (GEWaSC)

ABSTRACT: Our goal is to develop a **G**enome-**E**nabled **Wa**tershed **S**imulation **C**apability (**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 functioning, and how these interactions co-evolve. This calls for dramatically new simulation capabilities that couple microbial functional distribution with a suite of biogeochemical and hydrologic processes. These new simulation capabilities will go beyond conventional watershed models by ultimately integrating surface hydrologic, biogeochemical, and microbial processes (e.g., those taking place in the soil and surface waters) with the subsurface flow, transport, and reaction in a formal manner to provide a complete description of carbon, biogeochemical, and nutrient cycles within a catchment. A novel feature of the GEWaSC will be the coupling of microbial functional distributions inferred from trait-based models that are parameterized using site-specific “omic” data with a comprehensive simulation of biogeochemical networks. In addition, the GEWaSC model for flood plain to watershed scale cycling will rely on model development and quantification of vertical carbon and nutrient fluxes from the vegetative canopy, soil zone, and deeper vadose zone to the water table. These will provide boundary conditions for water flow and carbon/nutrient flux to the groundwater, and the basis for process models that can quantify these fluxes dynamically. Detailed process models for the interactions of organic matter and mineral surfaces and their effect on carbon and electron fluxes, along with data on organic carbon speciation and biogeochemical reaction rates, will be used to further refine the fate of organic carbon and nutrients within the flood plain and ultimately the watershed. In addition, new methods for treating the multiscale nature of the watersheds will be necessary, since fully resolved methods are not computationally feasible in all cases. In the later phases of this project, a new multiscale framework will be developed that can incorporate parameters and processes from the microscale (whether defined in terms of pore-scale soil processes, or in terms of subcatchment vegetation, exposure, and soil-type zones) into watershed-scale simulations. The guiding principle for the GEWaSC is that surface and subsurface hydrology provides the basis for model discretization because of its control of biophysical and biogeochemical connectivity. In this respect, surface and subsurface flow of water control the transport of organic carbon, nutrients, and the various electron acceptors and thus provide the first-order basis for definition of numerical model units. Despite the inability to completely resolve all of the relevant scales at the flood plain to watershed scale, high-resolution reactive transport modeling based on High Performance Computing (HPC) will be an important part of the GEWaSC effort. This framework will be used to develop an interpretive and predictive capability for the quasi-steady state biogeochemical and microbial functional zonation within a subsurface aquifer, as influenced by lateral groundwater flow and vertical inputs from the vadose zone.

NAME: Michael Wilkins
ORGANIZATION: Pacific Northwest National Laboratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Proteins in the subsurface - understanding microbial function and metabolism using proteogenomics

ABSTRACT: Identifying the active mechanisms that drive microbial biogeochemical cycles in subsurface environments is key for obtaining a better predictive understanding of both short-term and long-term system behavior. Shotgun proteomics, the analysis of all proteins within a sample, can be coupled with genomic information to reveal potential active pathways and organisms that catalyze reactions and processes of interest.

At the Rifle site in Western Colorado, this approach has been utilized to track *Geobacter* physiology and metabolism over a period of active carbon amendment to the subsurface. This biostimulation promotes the growth and activity of *Geobacter* strains that subsequently catalyze the reduction of both Fe(III) phases and U(VI). These species therefore play a key role in the subsurface cycling of metal cations. To investigate how *Geobacter* strains respond to increased carbon flux in the aquifer, twelve planktonic biomass samples were recovered using filtration over a 30-day period from a downgradient monitoring well. Across these samples, 16S rRNA analyses were used to track the rapid enrichment of *Geobacter* species; concomitantly, shotgun 2D-LC-MS/MS analyses identified approximately 1,200 proteins from dominant *Geobacter* species, and revealed active central metabolism pathways through acetyl-CoA and pyruvate that allowed the efficient use of acetate for growth and energy generation. Over the experimental period, we infer potential shifts in carbon flux from biomass synthesis to respiration, and note the activity of both hydrogenase and nitrogenase enzymes.

During a subsequent experiment that stimulated sulfate reduction within the Rifle aquifer, another series of temporally resolved biomass samples were recovered. Subsequent shotgun proteogenomic analyses have identified a significant phage signature in some samples, suggesting that viral predation may play a role in microbial community dynamics under certain conditions.

Most recently, background planktonic biomass samples have been recovered by filtering large volumes of groundwater. Coupled to metagenomic assemblies, analyses of proteins from these samples will aid the understanding of active biogeochemical cycles under non-stimulated conditions at the site, and link to modeling efforts that aim to predict microbially-catalyzed processes occurring at the floodplain scale.

NAME: Steve Yabusaki
ORGANIZATION: PNNL
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Field-scale simulations of engineered bioreduction: Super 8, proteomics, genome-scale metabolic modeling, and beyond

ABSTRACT: The 2010 Super 8 acetate biostimulation field experiment was the first at the Rifle IFRC site to test the response of metal-reducing bacteria to elevated levels of aqueous U(VI) and calcium. The introduction of high bicarbonate and sodium concentrations on the west side of the experimental plot resulted in observed aqueous uranium and calcium concentrations up to 4 times ambient concentrations. While we are interested in the effect of evolving geochemical conditions on the biologically-mediated metal reduction rates, it is particularly difficult to quantitatively discern the individual contributions of competing processes from the monitored concentrations alone. These species are directly involved in aqueous and surface complexation, microbially-mediated TEAP, and mineral reactions, which are sensitive to controls (e.g., pH, Eh, alkalinity, etc.) affected by other reactions. The simulation addresses these issues through systematically coupled process models that have been developed in the context of observed behaviors from multiple field experiments at this site. For this simulation, the flow model parameters were not calibrated; we simply used the previously defined sandy gravel lithofacies properties and drove the model with time-dependent observed water levels. With the exception of changing the dependence in the goethite bioreduction rate law from >FeOH to FeOOH, all reactions, thermodynamics, and rate laws were identical to the previously published simulation of the 2008 Big Rusty acetate biostimulation field experiment. The modeling explores a large range of sodium, bicarbonate, acetate, and uranium exposure due to the different injection locations and schedules, as well as the slight misalignment of the flow field and the well layout. The removal of U(VI) from solution is demonstrated to be a trade-off between the U(VI) bioreduction rate and enhanced adsorption to the recently vacated surface complexation sites.

The Super 8 experiment was also notable for the relatively large number of proteomic samples (5, 8, 10, 13, 15, 17, 29, 36, and 43 days) collected at the well least impacted by the bicarbonate injection, CD01. In this simulation, we replaced the Fe(III) TEAP reactions and rate laws with a genome-scale metabolic ("*in silico*") model for *Geobacter metallireducens* (748 intracellular and exchange reactions). The *in silico* model of physiological metabolic pathways was embedded in the eSTOMP field-scale modeling framework. A linear programming solver is used to calculate feasible limits of intracellular metabolic flux distribution under a constraint-based flux balance analysis. Over 900 proteins specific to *Geobacter spp.* were detected. The annotation of genome-specific proteins to individual metabolic pathway reactions enables the abundance of a specific detected protein to be used to assess a specific predicted reaction flux. The effect of evolving biological and geochemical conditions on the trade-off between biosynthesis and respiration pathways is examined.

Finally, we show a preliminary 3-D variably saturated flow and transport simulation of the entire Rifle site floodplain. This will provide the foundation for the upcoming exploration of the floodplain microbial community in the hydrologic context of the upland watershed and the Colorado River.

SUBSURFACE BIOGEOCHEMICAL RESEARCH

LAWRENCE LIVERMORE NATIONAL LABORATORY (LLNL)

NAME: M.A. Boggs
ORGANIZATION: Lawrence Livermore National Laboratory
PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: A Survey of Plutonium Sorption Behavior in Ternary Pu-DOM-Mineral Systems and Novel Spectroscopies to Probe Their Molecular Structure

ABSTRACT: The Subsurface Biogeochemical Research (SBR) Scientific Focus Area (SFA) at Lawrence Livermore National Laboratory is focused on identification and quantification of the biogeochemical processes that control the fate and transport of Pu. The second of five program elements is focused on quantifying the sorption/desorption behavior of ternary surface complexes at environmentally relevant Pu concentrations. Here, we present results of this program element as well as early results from our microbiological investigations.

We have studied the effect of Pu in the presence of montmorillonite with three organic ligands: humic acid (HA), fulvic acid (FA), and deferrioxamine B (DFOB). A decrease in Pu sorption relative to a ligand free system was observed over a wide pH range in systems containing HA and FA. The results suggest a relatively straightforward competition reaction between montmorillonite and HA for Pu complexation and a weaker influence of FA. Conversely, DFOB led to an increase in Pu(IV) sorption. Montmorillonite was able to sorb up to1 mM DFOB/g mineral. Both TEM and XRD indicated an increase in montmorillonite interlayer spacing from 10 to 18 Å with the addition of DFOB.

The unique behavior of the Pu(IV)-DFOB complex led to structural characterization studies by NMR which combined with UV-Vis identified two distinct complexes. Conversion between the two complexes was rapid as the pH shifted below or above ~ 4. ^{1}H spectra of the complexes show a large amount of peak broadening and chemical shifts which can be associated with changes in conformation and the presence of a paramagnetic metal center. Peak assignments were made through the 2D techniques of Correlation Spectroscopy (COSY) and Heteronuclear Single Quantum Correlation (HSQC). Variable temperature ^{1}H spectra were acquired and we were able to observe pseudo contact shifts (PCS) and determine the distance of the shifted protons from the metal center. Diffusion Ordered Spectroscopy (DOSY) was used to determine the rates of diffusion and size of the two Pu(IV)-DFOB complexes. These results indicate that the complex at pH 7.0 is on the order of twice the size of the lower pH complex. The high pH complex was previously identified[1] as Pu(IV)DFOB$(OH)_2$, while our results suggest that it is more likely a dimeric DFOBPu(IV)di-μ-OH-DFOBPu(IV) species.

Sorption of Pu(IV) to a number of other mineral surfaces in the presence of natural organic matter (NOM) was examined using a combination of batch sorption and Fourier Transform Infrared Spectroscopy (FTIR). Tritium labeled fulvic and humic acid and ^{14}C labeled citric acid were used to lower the NOM detection limits and observe sorption of NOM and ^{238}Pu simultaneously. In general, the results indicate the possibility of ternary surface complex formation at low pH which will enhance sorption relative to a ligand free system and solubilization of Pu at high pH due to aqueous complexation with

NOM. The formation of ternary complexes will require that NOM serve as a sorbed, bridging ligand. The existence of specifically sorbed NOM complexes has been examined and confirmed using FTIR.

Prepared by LLNL under Contract DE-AC52-07NA27344.

[1] Boukhalfa, H.; Reilly, S.; Neu, M., *Inorganic Chemistry* **2007,** *46*, 1018-1026.

NAME: Anne Kersting
ORGANIZATION: Lawrence Livermore National Laboratory
PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Quantifying Plutonium Sorption Affinities and Desorption Rates from Mineral Surfaces: A Numerical Approach to Modeling Batch/Flow-Cell Experimental Data and Implications to Field-Scale Plutonium Transport

ABSTRACT: The Subsurface Biogeochemical Research (SBR) Scientific Focus Area (SFA) at Lawrence Livermore National Laboratory ("Environmental Transport of Plutonium: Biogeochemical Processes at Femtomolar Concentrations and Nanometer Scales") is focused on identification and quantification of the biogeochemical processes that control the fate and transport of Pu at environmentally relevant (10^{-12} – 10^{-18} mol/L) actinide concentrations. The first of five program elements is focused on quantifying affinities and rates of binary sorption/desorption to mineral surfaces at environmentally relevant Pu concentration. Experiments are performed using batch/flow cell experimental techniques combined with LLNL's unique capability in measuring actinide concentrations at ultralow ($<10^{-14}$ mol/L) concentrations by AMS and characterizing the morphology of Pu associated with mineral surfaces (TEM/NMR). To date, we have examined Np(V)-goethite, Pu(IV/V)-goethite, and Pu(IV/V)-montmorillonite sorption isotherms over a ten order of magnitude Pu/Np concentration range. We have also used dynamic flow cell sorption/desorption experiments to quantify the kinetics of these reactions. A simple yet flexible numerical model has been developed to simulate the known Pu redox transformations occurring on the surface of minerals and quantify the various sorption, desorption, and redox transformation data collected to date. The model is based on our early efforts focused on modeling Np(V) sorption behavior on goethite [1]. However, the model was expanded to account for the surface-mediated Pu redox processes identified on mineral surfaces. In the case of Pu(V) interaction with goethite, we were able to fit our pH 8 batch sorption experiments and adsorption/desorption flow cell data, including the transient stop flow events, simultaneously. The simulated affinities and sorption/desorption rates are consistent with previous surface mediated reduction rates reported in the literature and measured aqueous and sorbed Pu oxidation states. Importantly, a kinetic hysteresis effect was essential to fitting the surface mediated redox reactions. The inclusion of this effect in the numerical model is consistent with the hysteresis term used in the earlier Np(V) model [1]. However, the hysteresis effect for Pu is much more pronounced and leads to desorption rates on the timescale of years. The rate limiting step in Pu desorption appears to be the slow oxidation of Pu(IV) on the mineral surface to Pu(V). The slow desorption rates suggest that observed colloid facilitated radionuclide transport may occur as a result of the relative stability of adsorbed Pu(IV). Similar behavior was observed in the case of Pu-montmorillonite experiments as a function of pH and actinide concentration.

Prepared by LLNL under Contract DE-AC52-07NA27344.

Reference:

[1] R.M. Tinnacher, et al., Geochim. Cosmochim. Acta 75, 6584 (2011).

SUBSURFACE BIOGEOCHEMICAL RESEARCH

OAK RIDGE NATIONAL LABORATORY (ORNL)

ORNL INTEGRATED FIELD-SCALE SUBSURFACE RESEARCH CHALLENGES (IFRC)

ORNL SCIENTIFIC FOCUS AREAS (SFA)

NAME: Craig Criddle
ORGANIZATION: Stanford University
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Field observation of uranium sequestration in iron-rich sediments under sequential reduction-oxidation conditions at the DOE Oak Ridge IFRC

ABSTRACT: At the U.S. DOE Oak Ridge Integrated Field Research Challenge (ORIFRC) site, the iron content of shallow subsurface materials (i.e. weathered saprolite) is relatively high (up to 5-6% by weight), and iron species play a critical role in the long-term sequestration of uranium. To assess the role of iron on U sequestration under field conditions, we monitored U(VI) levels in groundwater after pilot-scale bioreduction and reoxidation experiments conducted at the ORIFRC area 3 site, adjacent to the former S-3 disposal ponds (source zone). In a previous experiment to assess bioreduction, aqueous U(VI) concentrations at the site decreased to levels less than the EPA MCL following intermittent injection of ethanol as the electron donor. When the oxidants oxygen and nitrate were then allowed to enter the bioreduced zone, bioreduced U(IV) was oxidized resulting in a temporary rebound in aqueous phase uranium concentrations.

To understand the long-term effect of oxidant exposure, a field test was conducted with bioreduced sediments exposed to nitrate for more than 1,380 days within Area 3. Nitratecontaminated groundwater was allowed to enter a previously bioreduced zone via the natural groundwater gradient. The geochemical response to this contaminated groundwater was dependent upon the monitoring location: in general, nitrate concentrations entering the previously bioreduced area increased gradually from near zero to ~50-300 mM within 200 days then stabilized. The pH declined from levels of 6.2-6.7 following bioreduction to <5.0. Uranium concentrations rebounded in all monitoring wells but at different rates. At most locations, U concentrations rebounded, declined, then rebounded a second time. Methane gas disappeared while N2O levels increased dramatically (from levels below detection to 20,000 - 44,000 ppmv) at monitoring wells subject to three years of niitrate exposure.

The U(IV) in sediments was mainly reoxidized to U(VI) species. XANES analyses indicated that the dominant form of uranium after re-oxidation was a mixture of uranyl carbonate and U(IV) bound to Fe bearing phases. The U content in the sediments remained as high as that measured after bioreduction, indicating that much of the U remained sequestered *in situ*. SEM observations of surged fine sediments revealed clusters of colloidal-sized precipitates (200-500 nm) containing uranium. These particles appeared to have formed in situ, and were present in a control area that received no ethanol addition and in previously bioreduced sediment. XRF analyses of sediment sampled after after three years of oxidation revealed that the U content on previously bioreduced sediment was as high or higher than values measured just after bioreduction, ~2000 mg/kg, indicating long-term U sequestratration in pre-bioreduced sediments. The microbial community before and after the re-oxidation was also analyzed to elucidate the impacts of geochemical changes on subsurface microbiology.

NAME: Baohua Gu
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Geochemical Controls on the Immobilization of Metals and Radionuclides and Microbial Activity in a Highly Contaminated, Acidic Aquifer

ABSTRACT: Few effective remedial technologies exist to remove or immobilize uranium *in situ* in a highly contaminated acidic aquifer at the Integrated Field Research Challenge (IFRC) site in Oak Ridge, Tennessee. This research was conducted to evaluate geochemical pH controls on chemical speciation and immobilization of contaminant metal ions and radionuclides and microbial activity in both laboratory and field studies. We performed laboratory batch/column and field titrations and geochemical modeling to better understand and quantify the reactions governing the speciation and fate of contaminant metals and radionuclides in the subsurface. We show that the addition of strong base can provide a rapid yet effective means of sequestering U(VI), Tc(VII), and other toxic metals such as Cr(VI) and Co(II) in the soil and groundwater. Greater than 94% of soluble U(VI) can be immobilized at pH above 4.5 by the co-precipitation and/or adsorption with Al-oxyhydroxides, and the presence of sediment minerals facilitates the immobilization of these contaminants. An extended geochemical model with fewer adjustable parameters described well the concentration and speciation of metal ions and precipitates in these titration studies. In > 1-year field plot studies, the pH of recirculated groundwater was slowly increased from an ambient value of approximately 3.5 to about 5.5 in the injection well, and we observed corresponding decrease in U(VI) and Al (> 90% reduction), confirming our laboratory observations. Downgradient wells and the extraction well have shown similar behavior with approximately 80% decrease in U(VI) and Al, despite the fact that the extraction well did not exhibit a discernible change in pH. The response of the groundwater microbial communities was investigated on a monthly basis. The abundance and activity of microorganisms (oxygen consumption, denitrification) generally decreased with time in wells in which the pH substantially increased from base addition. Wells that showed a slower response to bromide tracer tests (FW115, FW130) exhibited a more variable response or no response to base addition in agreement with the smaller pH changes observed in these wells. Microbial communities are well adapted to moderately acidic pH in the OR-IFRC subsurface after decades of exposure to acidity. An elevation of pH could thus act as a stressor that inhibits microbial activity over the short term, or base addition may have unintended consequences for microbial communities. Nevertheless, our results indicate that the field plot acted as a barrier (or a sorbent) for Al, U(VI) and other toxic metals, thus validating our original hypothesis that the master variable for U(VI) and metals attenuation and microbial activity is pH. Aluminum hydrolysis and the presence of carbonates are the dominant pH buffering reaction impeding U and toxic metal precipitation and adsorption at Oak Ridge IFRC.

NAME: Andre Revil
ORGANIZATION: Colorado School of Mines, Department of Geophysics, Golden, 80401, CO, USA
PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Geochemical and geophysical responses during the infiltration of fresh water into the contaminated saprolite of the Oak Ridge Integrated Field Research Challenge site, Tennessee

ABSTRACT: At the Oak Ridge Integrated Field Research Challenge (IFRC) site, Tennessee, the saprolitic aquifer was contaminated by past leaks from the former S-3 disposal ponds between 1951 and 1983. The chemistry of the contaminant plume is also episodically impacted by fresh meteoritic water infiltrating vertically from a shallow variably saturated perched zone and the ditch surrounding the former S-3 ponds. We performed a column experiment using saprolite from the contaminated aquifer to understand the geochemical and complex electrical conductivity signatures associated with such events. The changes in the pH and pore water conductivity are responsible for measurable changes in both the in-phase and quadrature conductivities. The pore water conductivity can be related to the nitrate concentration (the main ionic species in the plume) while the release of uranium is controlled by the pH. We developed a simple model to determine the pore water conductivity and pH from the recorded complex conductivity. This model is applied to time-lapse resistivity data at the IFRC site. Time-lapse inversion of resistivity data in the field shows the occurrence of an infiltration event during the winter of 2008-2009 with a dilution of the pore water chemistry and an increase of the pH. A simple numerical simulation of the infiltration of fresh water into the unconfined contaminated aquifer is consistent with this scenario.

NAME: Guoping Tang
ORGANIZATION: ORNL
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: An Integrated Experimental and Modeling Study of U(VI) Bioreduction with Emulsified Vegetable Oil as Electron Donor from Laboratory to Field Scales

ABSTRACT: Bioreduction and immobilization of U(VI) in contaminated sites with simple substrates such as acetate and ethanol require daily to weekly injection to avoid reoxidation and remobilization. We hypothesized that slowly degraded and strongly retained substrates could lead to longer term U(VI) reducing conditions, therefore, decreasing the injection frequency from daily/weekly to monthly/quarterly. To test this hypothesis, we conducted microcosm and field tests with emulsified vegetable oil (EVO) as a slow release substrate, and developed a comprehensive model to quantify the microbiological and geochemical dynamics observed in these tests.

In these tests, EVO supported microbial reduction of nitrate, Fe(III), U(VI), and sulfate and CO_2 (methane production observed). In the field test, a single 2-h EVO injection resulted in decreased U concentration downstream (~50 m) by 80% for 100 days, and U discharge to a nearby creek by 50% for over 1 year. X-ray adsorption near edge spectroscopy (XANES) analysis of aquifer solids confirmed U(VI) reduction to U(IV). Pyrosequencing and quantitative PCR of 16S rRNA from monitoring well samples revealed a rapid decline in bacterial community richness and diversity, and indicated the selection of a narrow group of taxa rather than abroad community stimulation after EVO injection. Based on the relative abundance of representative operational taxonomic units observed through DNA sequencing approaches, and known physiologies of closely allied species or genera, we developed a conceptual model in which *Pelosinus* catalyzes oil hydrolysis and ferments glycerol, *Desulforegula* oxidizes long-chain fatty acids, and *Comamonadaceae*, *Geobacter*, and *Desulfovibrio* reduce nitrate, Fe(III), U(VI), and sulfate, and *Methanobacteria*, and *methanomicrobia* growth leads to methane production.

We implemented the conceptual model in a numerical biogeochemical model, which includes hydrolysis of EVO, production and oxidation of long-chain fatty acids (LCFA), glycerol, acetate, and hydrogen, reduction of nitrate, Fe(III), U(VI) and sulfate, and methanogenesis with growth and decay of multiple functional microbial groups. We parameterized the biogeochemical model by using growth rate parameter values from the literature and estimating EVO, LCFA and glycerol degradation rate coefficients based on microcosm test results.

Using a kinetic Langmuir isotherm to approximate EVO retention, we applied the biogeochemical model to simulate observed acetate, nitrate, Fe, U, and sulfate concentration dynamics, and the activities of multiple microbial functional groups during and after EVO injection. When the lab-determined parameters were applied in the field-scale simulation, the estimated rate coefficient for EVO hydrolysis was about 1 order of magnitude greater than that in the microcosms. Model results suggested that precipitation of LCFA with Ca in the groundwater created a secondary long-term electron donor source. The model predicted substantial accumulation of denitrifying and sulfate-reducing bacteria, and U(IV) precipitates. The accumulation was greatest near the injection wells and along the lateral boundaries of the treatment zone where electron donors mixed with electron acceptors in the groundwater. While electron acceptors such as sulfate have generally been considered to compete with U(VI) for electrons, this work highlighted their role in providing electron acceptors for microorganisms to degrade complex substrates thereby enhancing U(VI) reduction and immobilization.

NAME: David Watson
ORGANIZATION: Oak Ridge National Laoratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Hydrobiogeochemical Interactions along “Flow Tubes” Controls Watershed Scale Contaminant Flow and Transformation at the Oak Ridge IFRC

ABSTRACT: Geochemical, spectrographic, microbiological and hydrogeologic studies at the ORIFRC site indicate that groundwater transport in structured media may behave as a system of parallel flow tubes. These tubes are preferred flowpaths that enable contaminant transport parallel to bedding planes (strike) over distances of 1000s of meters. A significant flux of groundwater is focused within an interval defined by the interface between the competent bedrock and overlying highly-weathered saprolite, commonly referred to as the "transition zone." Characteristics of this transition zone are dense fractures and the relative absence of weathering products (e.g. clays) results in a significantly higher permeability compared to both the overlying clay-saprolite and underlying bedrock. Several stratabound low seismic velocity zones located below the transition zone were identified during geophysics studies and were also determined to be fractured high permeability preferred contaminant transport pathways during subsequent drilling activities. XANES analysis of precipitates collected from these deeper flow zones indicate 95% or more of the U deposited is U(VI). Linear combination fitting of the EXAFS data shows that precipitates are ~51±5% U(VI)-carbonate-like phase (e.g., liebigite) and ~49±5% U(VI) associated with an iron oxide phase; inclusion of a third component in the fit suggests that up to 15% of the U(VI) may be associated with a phosphate phase or OH^- phase (e.g.,schoepite). Although precipitates with similar U(VI)-carbonate and/or phosphate associations were identified in the transition zone pathways, there were also U(VI) complexes adsorbed to mineral surfaces that would tend to be more readily mobilized. Groundwater in the different flow tubes has been determined to consist of different water quality types that vary with the solid phase encountered (e.g., clays, carbonates, clastics) as contaminants migrate along the flow paths. This lateral and vertical variability in geochemistry, particularly pH, has a significant impact on microbiological community composition and activity. Ribosomal RNA gene analyses coupled with physiological and genomic analyses suggest that bacteria from the genus *Rhodanobacter* (a diverse population of denitrifiers that are moderately acid tolerant) have a high relative abundance in the acidic source zone at the ORIFRC site. Watershed-scale analysis across different flow paths/tubes revealed strong negative correlation between pH and the absolute and relative abundance of *Rhodanobacter*. Recent studies also confirmed that the ORIFRC site hosts a diverse fungal community, with significant differences observed between acidic (pH <5) and circumneutral (>5) wells. The lack of nitrous oxide reduction capability in fungi, and the detection of denitrification potential in slurry microcosms suggest that fungi may have a heretofore underappreciated role in biogeochemical transformations, with implications for site remediation and greenhouse gas emissions. Further research is needed to determine if these organisms can influence U(VI) mobility either directly through immobilization or indirectly through the depletion of nitrate. In conclusion, additional studies are required to quantify the processes (e.g., solid phase reactions, recharge, diffusion, microbial interactions) that are occurring along the groundwater flow tubes identified at the ORIFRC so predictive models can be parameterized and used to assess long-term contaminant fate and transport and remedial options.

NAME: Dwayne Elias
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Mercury Methylation: Microbial Species and Communities Involved in Hg Transformations (ORNL Hg SFA, Microbial Genetics and Transformations)

ABSTRACT: The discovery and verification of the mercury metyhylation genes, *hgcAB*, has been a seminal discovery by the ORNL Hg SFA. Their discovery now opens up new avenues of research. We have examined microbial communities involved in mercury methylation in streams receiving Hg from the Y12 plant at Oak Ridge in collaboration with the Field Task. Microcosm studies suggested active methylation downstream, with this activity being stimulated by the addition of sulfate or the carbon sources lactate, ethanol, methanol, or acetate. Both molybdate and cellobiose inhibited methylation activity. Water and sediment samples were analyzed for the microbial community complement phylogenetically via 454 pyrosequencing of the 16S rDNA gene V4 region. As expected, the addition of cellobiose stimulated the *Firmicute* population which has not been traditionally recognized as being able to participate in methylation while at the same time the delta-Proteobacteria population decreased, which has been repeatedly implicated in Hg-methylation. However, our recent discovery of the methylation genes led us to predict that both *Firmicutes* and methanogens are capable of this activity. Further inspection of the 16s rRNA sequences revealed that the *Firmicutes* stimulated did not possess the *hgcAB* genes and therefore explains the decreased methylation activity. However, this analysis did show that the relative abundance of methanogens that possess the *hgcAB* genes was increased. This suggests that, although the latter population increased in abundance, their methylation activity is low. This was infact the case when our predictions were tested and revealed that all predictions for methylators and non-methylators were accurate, but that the methylating rate and yield for the *Firmicutes* and methanogens was far below that of the delta-Proteobacteria.

Efforts are now underway to optimize universal methylation gene primers and quantitative primers for accurate quantification of the methylation potential of any environment. We are now also determining; 1) the presence of the native function of these genes as well as 2) the remainder of the biochemical pathway that is/may be used to route carbon and electrons in the absence of mercury. Work is also ongoing to better understand the expression and abundance of these genes by determining and characterizing the promoters and regulators of these two genes.

NAME: Baohua Gu
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Profiling mercury binding functional groups in natural organic matter and methylating bacteria

ABSTRACT: Recent studies have emphasized the crucial role of organic 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 reduced dissolved organic matter (DOM) results in both reduction of Hg(II) and oxidation of Hg(0), depending on the Hg/DOM ratios, and suggests the involvement of two competing mechanisms: reduction by reduced semiquinones and oxidation by thiol-induced oxidative complexation. Similar behaviors of reduction, oxidation, and surface binding of Hg species have also been observed on mercury-methylating microorganisms, such as *Geobacter sulfurreducens PCA and Desulfovibrio desulfurricans ND132*. As a key aspect of studying these processes, a robust and sensitive analytical approach for quantifying the organic thiols present in DOM and bacteria is needed. However, the analysis of organic thiols is not straightforward, primarily due to their low abundance, susceptibility to chemical and photo-chemical oxidation, and the inherent absence of distinguishing spectroscopic characteristics. To overcome these problems, we have utilized a chemical probe with thiol-specific fluorogenic labeling properties. We systematically evaluated the optimum labeling conditions for model thiols (cysteine and glutathione) with the goal of minimizing alterations to the bacteria and DOM samples, while ensuring high sensitivity (nanomolar levels) and selectivity for organic thiols, even in the presence of potentially interfering compounds (e.g., cystine, amino and carboxyl containing non-thiol compounds). We applied the optimized technique for the measurement of total thiols in washed cells of *Geobacter sulfurreducens PCA* directly in phosphate buffered saline solution and a complex DOM sample. Furthermore, we have developed an HPLC-fluorescence method, with detection based on the described fluorogenic labeling procedure, by which the individual thiols in DOM can be resolved from the other components of these complex mixtures, thereby allowing us to measure the individual thiolated compounds. We demonstrate this method for profiling organic thiols in DOM. A clearer understanding of the diversity (or lack thereof) of the major thiols in DOM can be useful for predicting the impact of Hg-DOM complexation, as it pertains to Hg uptake by methylating bacteria, as well as other mechanisms of Hg transformation in the environment.

NAME: Baohua Gu

ORGANIZATION: Oak Ridge National Laboratory

PROGRAM AFFILIATION: SBR

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

ABSTRACT: Mercury (Hg) is a persistent environmental pollutant that bioaccumulates in the form of neurotoxic methylmercury and affects human health. Its redox cycling in anoxic environments critically links to the bioavailability of Hg for microbial uptake and methylation, but factors that affect this process are poorly understood. We study the kinetics of Hg reduction, oxidation and species transformation mediated by both abiotic and biological processes under dark, anaerobic conditions. Both reduction and surface complexation of Hg(II) were found to occur simultaneously on *G. sulfurreducens* PCA cells. Reduction of Hg(II) to elemental Hg(0) initially followed a pseudo-first order kinetics with a half-life of < 2 h in phosphate buffer (pH 7.4) solutions. However, cell surface complexation of Hg(II) was found to compete with and inhibit Hg(II) reduction by cells. This inhibitory effect is attributed to strong binding of Hg(II) via the sulfhydryl (-SH) functional groups on cell surfaces, similarly to reactions between Hg and natural organic matter (NOM) and thiol compounds. NOM simultaneously reduces and oxidizes Hg because of the presence of both reducing moieties (such as semiquinones) and thiol-containing functional groups in NOM. Using several strains of bacteria within the genera *Desulfovibrio* and *Geobacter* spp., we found that certain bacteria can also methylate Hg via anaerobic Hg(0) oxidation. *Desulfovibrio desulfuricans* ND132 was able to both oxidize and methylate Hg(0) in washed cell assays, with an observed initial methylation rate constant of up to $1.3\text{x}10^{-3}$ h^{-1}.*Desulfovibrio alaskensis* G20 can oxidize Hg(0) but not methylate mercury. *Geobacter sulfurreducens* PCA showed little Hg(0) oxidation and methylation activity under the same experimental conditions, but amendment with cysteine led to substantially enhanced oxidation and subsequent methylation. Our findings highlight several distinct and competing cell surface interactions, including reduction, oxidation, and complexation, under which microbial Hg(II) uptake and methylation occur. These observations could therefore have important implications for geochemical cycling of Hg and methylmercury formation in the natural environment. Our observations also demonstrate that, contrary to expectation, reduction of Hg(II) to Hg(0) does not necessarily prevent Hg uptake and microbial methylation.

NAME: Alexander Johs
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: The Genetic Basis of Bacterial Mercury Methylation

ABSTRACT: Mercury is a pervasive global pollutant which, as methylmercury, bioaccumulates in the food web and is highly toxic to humans and other organisms. Methylmercury is produced in natural environments from inorganic mercury, predominantly by anaerobic microorganisms. Sulfate-reducing bacteria are the main producers of methylmercury, although iron-reducing bacteria and methanogens can also be involved. Mercury methylation is an enzyme-catalyzed process proposed to be associated with the reductive acetyl-CoA (Wood-Ljungdahl) pathway and potentially linked to corrinoid proteins involved in this pathway. However, no direct evidence firmly connects the acetyl-CoA pathway and the ability of bacteria to methylate Hg. Furthermore, phylogenetic analyses have not revealed any distinctive trends or clustering of methylating versus non-methylating microorganisms. Thus, despite substantial effort, the genetic and biochemical basis of microbial mercury methylation has remained elusive for over 40 years.

A combination of chemical reasoning, genomics, and microbiology lead to the discovery of a two-gene cluster, *hgcA* and *hgcB*, required for mercury methylation by *Desulfovibrio desulfuricans* ND132 and *Geobacter sulfurreducens* PCA. In either bacterium, deletion of *hgcA*, *hgcB* or both genes abolishes mercury methylation. The genes encode a putative corrinoid protein, HgcA, and a 2[4Fe-4S] ferredoxin, HgcB, consistent with roles as a methyl carrier and an electron donor required for corrinoid cofactor reduction, respectively. This two-gene cluster is present in all known methylating bacteria and archaea but absent in non-methylators. Homologs have been found in the genomes of more than 50 diverse microorganisms, suggesting a common mercury methylation pathway among bacteria and archaea with sequenced genomes. The identification *hgcA* and *hgcB* is a critical step toward identifying sources of microbial methylmercury production in the environment.

NAME: Carrie Miller
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Factors influencing sediment methylmercury concentrations in a mercury-contaminated creek

ABSTRACT: East Fork Poplar Creek (EFPC), originating within the Y-12 National Security Complex (Y-12) in Oak Ridge, TN, USA, has elevated mercury concentrations as a result of historical Hg use at the facility. Stream water total mercury (HgT) concentrations decrease downstream but over this same reach methylmercury (MeHg) concentrations increase. To examine processes controlling the concentration of MeHg in this system, sediment cores were collected quarterly at two locations 17 km apart in EFPC between October 2010 and August 2012. MeHg sediment concentrations were most highly correlated ($p<0.001$) with organic carbon content, Fe(II) and reduced inorganic sulfur. In sediment cores collected at the upstream site sandy, coarse grain sediment mixed with fine grain material dominated and at this sitedown core changes in redox sensitive parameters (Fe(II) and reduced S) were not observed. Fine grain sediments dominated in cores from the downstream site and the concentration of Fe(II) and reduced S showed increased with depth down core. At this site, mercury methylation potentials (MMP), measured using enriched stable isotopes of Hg, were higher than the upstream site. Seasonal differences in MMP, with the highest potentials measured in April, were observed in cores from the downstream site but not the upstream site. Although differences in MMP were observed between the two sites there was no significant difference in the ambient sediment MeHg concentrations. No clear differences in demethylation potential were found between sites or seasons in the creek sediment cores. Sediment cores were also collected from an ephemeral stream running through the EFPC floodplain at the upstream site and these cores were collected even when the stream was stagnant or dry. In core samples collected in October 2011 and January 2012, high concentration of MeHg were measured but methylation potentials were low suggesting MeHg production and subsequent accumulation in floodplain soils. In April 2012 ambient MeHg concentrations in the floodplain soils were lower than October and January but methylation potentials were higher. This suggests that MeHg had been transported out of the floodplain soils during the wetter winter months, conditions favoring demethylation had developed, or a combination of both factors were occurring. At the downstream main channel creek site and in the floodplain ephemeral stream seasonally driven differences in temperature, which can influence microbially driven redox processes, appear to strongly influence MeHg cycling. Within the floodplain stream soil saturation status is another important factor controlling MeHg concentrations and production

NAME: Ami RIscassi

ORGANIZATION: Oak Ridge National Lab

PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Storm dynamics of Hg and MeHg in East Fork Poplar Creek: What can it tell us about transport and source areas of Hg and MeHg within the catchment?

ABSTRACT: East Fork Poplar Creek (EFPC) in Oak Ridge, TN currently receives a steady supply of inorganic Hg (~50-150 ng/L) from its headwaters due to historic contamination. Stream sediment and adjacent floodplain soils downstream have a wide range of elevated levels of Hg (5-40 mg/kg dw) and methylmercury (MeHg) (1-30 µg/kg dw). It is unclear if floodplain MeHg is a dominant contributor to the creek, which has steadily increasing concentrations of MeHg downstream. We investigate the variability in stream Hg and MeHg with changes in discharge and corresponding hydrologic connectivity between the creek and surrounding floodplains to elucidate origins of watershed Hg and MeHg contributions downstream and factors that affect mobilization.

From March 2012 through March 2013 four high-flow events were sampled along rising, peak and falling limbs of each storm hydrograph in Spring, Summer, Fall and Winter seasons. Monthly baseflow samples were also taken. The range of discharge conditions sampled (n=124 to date) is approximately 20 cfs (summer baseflow) to 4100 cfs. Samples were analyzed for filtered and unfiltered Hg and MeHg, dissolved organic carbon (DOC), UV-vis spectra, anions, metals and total suspended solids (TSS). During all storms particulate Hg and MeHg concentrations increase directly with TSS, approximately 12 ng Hg and 0.013 ng MeHg per mg TSS (r^2=0.92 and 0.78, respectively). Similar to most non-industrially contaminated systems, dissolved Hg (HgD) increases in synch with DOC concentration for all events (r^2=0.71). These results suggest that DOC is an important transporter of watershed Hg even with the high Hg/DOC ratio at our site (~ 7 ng Hg per mg DOC as compared to 0.2-0.7 ng Hg per mg DOC reported for systems receiving Hg primarily from atmospheric deposition). Unlike HgD, dissolved MeHg (MeHgD) dynamics were not consistent for all events, decreasing in concentration during the two larger events and remaining stable for the smaller storms revealing floodplain soil water mobilized during storms is not a transport mechanism that increases in-stream MeHgD concentrations. Future analysis will evaluate both storm specific and seasonal MeHg and Hg patterns in relation to all other water quality parameters as well as discharge.

SUBSURFACE BIOGEOCHEMICAL RESEARCH

PACIFIC NORTHWEST NATIONAL LABORATORY (PNNL)

NAME: Xingyuan Chen
ORGANIZATION: Pacific Northwest National Laboratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Improving the reactive transport modeling at the Hanford 300 Area with a Bayesian data assimilation framework

ABSTRACT: Data assimilation is an important tool to enhance the interactions between the field and lab experiments and system-scale model developments. The ultimate goals are to advance our understanding of the system and reduce the uncertainty in model predictions. We demonstrate a Bayesian data assimilation framework that can integrate information from different sources in a sequential manner, using the reactive transport modeling at the Hanford 300 Area as an example.

Flow and transport processes within the Hanford 300 Area are impacted by the extremely dynamic groundwater-riverwater exchange with the adjacent Columbia River and heterogeneous distribution of source terms within the site. To improve the accuracy of reactive transport modeling at the site, it is essential to reduce the hydrologic uncertainty (transient flow boundary conditions and the underlying heterogeneous hydraulic conductivity field) and geochemical uncertainty (geochemical reaction processes and parameters, and heterogeneity in initial uranium distributions). We reduced such uncertainties by assimilating multiple types of data obtained from various field experiments conducted at the Hanford 300 Area. In the hydrologic data assimilation step, data from constant-rate injection tests, borehole flowmeter profiling, and conservative tracer tests, are sequentially assimilated across scales using a combination of Bayesian techniques to reduce uncertainty in the estimated permeability field. The hydrologic data assimilation is then followed by geochemical data assimilation, where the goal is to infer the initial condition and geochemical parameters, such as sorption sites and reaction rates, by assimilating breakthrough curves of a reactive tracer observed during adsorption/desorption field experiments. The computational demand was managed by using the multi-realization capability within the parallel PFLOTRAN simulator. The Bayesian data assimilation framework has been shown to be efficient and effective in integrating multiple types of data for uncertainty reduction and improving model predictions.

The general data assimilation framework we developed in this study can be readily applied to integrate model developments and field experimental data in other complex systems at various scales. In future studies, we will apply this framework to study a coupled hydro-biogeochemical model (including C/N cycling and microbial community dynamics) in the dynamic groundwater-river water interaction zone in the Hanford 300 Area, integrating multiple types of spatio-temporal data, such as microbial community, geochemistry, hydrological and geophysical measurements, and others.

NAME: Glenn Hammond
ORGANIZATION: Pacific Northwest National Laboratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: System Scale Imaging and Modeling of Groundwater-River Water Exchange at the Hanford 300 Area

ABSTRACT: System-scale groundwater-river water exchange at the Hanford 300 Area is being measured and modeled to study its impact on groundwater geochemistry and microbial populations at the site. Groundwater flow and biogeochemical transport within the Hanford 300 Area are strongly coupled and exhibit complex behavior as the river stage fluctuates due to seasonal loading and daily upstream dam operations. As a result, the water table rapidly fluctuates causing river water to enter, mix with groundwater, and recede from the aquifer. The mixing process impacts water chemistry and subsequently microbial populations and activities at the site because river water chemistry and microbiology differs significantly from that of the groundwater. The mixing also directly impacts the migration of contaminants at the site.

River water intrusion is being monitored with an array of continuous pressure, temperature, and specific conductance probes installed in wells. In addition, large-scale (300 m x 300 m) 3D electrical resistivity tomography (ERT) has been deployed to monitor river water intrusion using a novel time lapse ERT imaging methodology that explicitly accommodates the water table contrast, providing 3D images of river water intrusion at a temporal resolution of three images per day. The ultimate objective of this research is to invert for hydrologic parameters within a system scale model of the site by assimilating data from the well sensors and ERT monitoring array. A Bayesian data assimilation framework is being used that requires the execution of ensembles of simulations. To address the computational demands, we are coupling PFLOTRAN (Hammond et al, 2012) with E4D (Johnson et al., 2010) to provide a parallel multiphysics (fluid flow, solute transport, and current flow) capability to simulate all field data. The optimized hydrologic model will be used as the base flow model for the PNNL SFA's biogeochemical transport modeling effort where PFLOTRAN will further be employed to simulate the fate and transport of microbial populations at the site.

Accomplishments of this research will include the development of a parameterized system scale model that can be used to (1) predict variably saturated flow and biogeochemical transport within the Hanford 300 Area given future river water and groundwater elevation measurements and geochemistry, (2) determine ecological processes controlling microbial populations within the site, and (3) assess indirect climatic impacts to biogeochemical cycles within the domain. The research will also demonstrate a novel inverse method for incorporating geophysical data in hydrologic parameter estimation.

NAME: Chongxuan Liu
ORGANIZATION: Pacific Northwest National Laboratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Development of Reaction-based Process Models for Complex Subsurface Systems

ABSTRACT: Geochemical and biogeochemical processes occur fundamentally at the pore-scale that can be described using reaction-based models. A major challenge to develop reaction-based process models for complex subsurface systems is that reaction rates and other parameters change as they are extrapolated from the pore to large scales. The scale-dependent behavior is caused by the heterogeneous distribution of reaction properties including sediment surface area/reactivity, microbial community assemblage and enzymatic functions, and transport properties that affect the supply and removal of reactants and/or reaction products. While large scale heterogeneity such as geological formations and facies may be explicitly considered in a reactive transport model, subgrid heterogeneity that is often below characterization resolution is a major source of model prediction uncertainty. In this poster, we will present approaches to scale reaction properties measured in the laboratory for field scale applications, and to minimize model prediction uncertainties caused by subgrid heterogeneity. The U(VI) sorption/desorption process in Hanford 300A sediments will be used as an example.

A set of column experiments with different sediment packing structures to mimic field scale subgrid heterogeneity were performed, and the experimental results were used to evaluate scaling approaches. A statistical approach based on grain-size distribution was developed to estimate field-scale reaction properties and their uncertainty including sediment surface site concentration/reactivity, organic carbon content and microbial respiration rates, and U(VI) sorption/desorption rate constants. The reaction properties in sediments are assumed to correlate with grain size distribution and be linearly additive with respect to grain size mass fractions in this approach. Once the reaction properties are determined for individual grain size fractions, the reaction properties at the field-scale can be estimated from the grain-size distribution data, which are easier to obtain than the reaction properties. Comparison of model simulations with experimental results indicated that a sub-grid, multi-domain treatment of reaction properties can further reduce the prediction uncertainties caused by subgrid heterogeneity of hydrological properties. The result was confirmed using a micromodel experiment with in-situ measurements of reaction rates in heterogeneous porous media under variable flow conditions. The presentation will also discuss the future extension of scaling concepts and approaches to the development of reaction-based biogeochemical models for microbially mediated organic carbon degradation and CO_2 production in complex field systems.

This presentation is part of SBR/PNNL_SFA

NAME: Matthew Marshall
ORGANIZATION: Pacific Northwest National Laboratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Multi-system Analysis of Microbial Biofilms

ABSTRACT: Direct examination of natural and engineered environments has revealed that the majority of microorganisms in these systems live in structured communities termed biofilms. In addition to microbial cells, biofilms are comprised of a poorly characterized organic matrix commonly referred to as extracellular polymeric substance (EPS) that may play roles in facilitating 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 to be produced during microbial metal reduction. The juxtaposition 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 a combination of synchrotron-based X-ray and infrared (IR) microimaging techniques combined with high-resolution EM imaging and spectroscopies at the Environmental Molecular Sciences Laboratory (EMSL). The result is a high spatial resolution, complex chemical image of a biofilm community. To understand the pore-scale and community-scale structure of biofilms in complex, three-dimensional environments, X-ray microtomography was employed at sector 2BM of the Advanced Photon Source. We have imaged hydrated biofilms grown on multiple substrates at energies ranging from 13-18 keV and spatial scales of 0.7 and 1.4 µm/pixel to reveal the complex microstructure within a biofilm. In some tomography studies, contrasting agents were also added to enhance biofilm visibility. To investigate the micrometer- to nanometer-scale chemical signatures of biofilms, a cryo-sample preparation technique was employed to produce 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 that several differences existed between the cell surface and the EPS matrix. Concurrent with these studies, we used synchrotron-based IR to produce high-megapixel (6.28 Mp) datasets with IR spectral data showing the localizations of key biofilm components (*i.e.*, proteins, sugars, flavins, nucleic acids, lipids) to further construct our chemical image of biofilms. The integration of the pore-scale and community-scale structural studies of hydrated biofilms with the micrometer-to nanometer-scale chemical signatures of biofilms will provide 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. Department of Energy (DOE) Office of Science Early Career Research Program Award (DOE National Laboratory Announcement 10-395).

NAME: Jim McKinley
ORGANIZATION: Pacific Northwest National Laboratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: River Water Intrusion and Related Contributions of Contaminant U During Springtime Runoff Events at the Hanford Site SFA

ABSTRACT: The area near the Columbia River shore at the 300 Area is affected by large excursions in the elevation of the adjacent Columbia River. In the springtime, large, abrupt, and long-lasting fluctuations of as much as 3 m result from the influx of snowmelt from the large Columbia River catchment. These fluctuations in elevation cause proportional changes in the elevation of the water table, drive azimuthal fluctuations in the local groundwater gradient, and result in short-lived infiltration of river water into the aquifer and lower vadose zone. We used a combination of sediment analysis and daily groundwater sampling to test the hypothesis that the large springtime variation in groundwater elevation caused contaminant U, adsorbed to sediment in the lower vadose zone, to be added to the aquifer U plume. Groundwater sampling included the wells of the 300 Area IFRC well field, providing an estimate of lateral variation in U concentrations, river water infiltration, and site-specific variations in the hydrologic gradient and water table elevation. Well cuttings collected during well field construction were analyzed for bicarbonate extractable U (BCU), mineralogy, and porosity. Statistical analysis of the combined data was used to estimate the solid-phase inventory of U and its potential impact on the aquifer.

The regional north-northwest hydrologic gradient was perturbed by springtime rises in river elevation. At the IFRC (200 m from the river shore), the gradient reversed to north-northeast during elevation rise, and reverted to its normal heading during elevation fall. The extent of river water infiltration (as the fraction of river water mixed into the aquifer) was dependent on the magnitude of the river's elevation rise and the rate of elevation change. If the rise was gradual, the regional gradient restricted the infiltration of river water; conversely, abrupt elevation rises resulted in infiltration of river water across the IFRC, to a river water fraction greater than 90%. Water table excursions into the vadose zone resulted in increased dissolved U, but the distribution was heterogeneous across the site. The timing and stratification of U concentrations indicated that the U was contributed immediately upon saturation of the lowermost vadose zone. Compositional stratification also indicated that the river water intruded along the top of the aquifer, and that the aquifer was homogenized after the gradient reversion. A geostatistical model that included BCU showed that the U source was heterogeneously distributed, consistent with the observed heterogeneous distribution of increased U concentrations.

The results showed intrusion of river water at distances of over 200 m from the Columbia River, indicating the presence of a very extensive hyporheic zone at this location. The addition of U during changes in water table elevation indicated that water table rise contributed U and other solutes to the aquifer (which have not been captured by previous modeling studies). The seasonal change in river elevation drove a significant compositional exchange between groundwater and surface water, and could represent unexplored impacts on surface ecology.

NAME: William Nelson
ORGANIZATION: Pacific Northwest National Laboratory
PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Effect of Floodplain-Scale Processes on Microbial Community Structure and Function

ABSTRACT: Genomic and metagenomic techniques are being used to study temporal and spatial variability of bacterial and archaeal communities in the Hanford Site 300 Area in relation to hydrologic and geologic features. Although 16S rRNA analyses of groundwater microbial populations collected over a 9-month period from 300 Area wells has revealed dynamic microbial community membership, the environmental factors responsible for driving this behavior are less well understood. Shotgun metagenomic sequence has been collected from four wells extending across the breadth of the 300 Area Integrated Field Research Challenge area. Co-assembly of collected sequences yielded 11,119 contigs >5000bp in length. Contiguous assemblies were sorted into 105 putative taxonomic bins using emergent self-organizing maps of nucleotide composition data coupled with read abundance data. Taxonomic evaluation of the binned sequences is in good agreement with pyrotag analysis previously done on these samples. A metabolic reconstruction of the individual bins and the entire community is underway to elucidate microbial interactions in the community. Single cell genomic techniques were employed to identify metabolic roles for *Pedobacter* species that exhibited significant fluxes in relative abundance over this time period, ranging from 0-14% of the community. Cells were desorbed from Hanford formation sediments, isolated using Fluorescent Activated Cell Sorting (FACS), and then single-cell genomic DNA was amplified using Multiple Displacement Amplification (MDA). Screening of single cells via 16S rRNA analyses was used to identify four *Pedobacter* cells for further whole genome shotgun sequencing. Reconstructed genomes were annotated, and estimates of genome completeness were inferred from single-copy gene identifications; these values ranged from 20-75%. Further analyses of these microorganisms indicate that they are chemoheterotrophic, with the ability to degrade complex organic polymers such as xylan. In addition, they may tolerate more microaerophilic niches in the subsurface via the use of cytochrome *cbb*$_3$-type terminal oxidases. These inferences suggest that possible fluctuations in organic carbon content in groundwater may play a role in driving abundance shifts in *Pedobacter* in the Hanford subsurface.

This research is part of the SBR SFA at Pacific Northwest National Laboratory.

NAME: Eric Roden
ORGANIZATION: University of Wisconsin-Madison
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Microbial chemolithoautotrophic oxidation of pyrite at circumneutral pH

ABSTRACT: Pyrite is present in significant abundance in Hanford 300 area (300A) sediments, and understanding oxidation pathways of this mineral can lend insight into the potential for production of ferric iron and sulfate, whose fate may impact contaminant mobility and overall biogeochemical cycling. The ability of microorganisms to catalyze the oxidation of pyrite (FeS_2) at circumneutral pH is poorly understood, despite the fact that this an energetically favorable process analogous to various well-known chemolithotrophic pathways (e.g. ferrous iron, sulfide, and elemental sulfur oxidation). Neutral pH abiotic oxidation of pyrite by oxygen has been extensively studied; however, there is virtually nothing known about the capacity for microorganisms to compete with abiotic reactions or enhance rates of pyrite oxidation at circumneutral pH.

This study examined the potential for microorganisms in Hanford 300 Area sediments to oxidize synthetic framboidal pyrite with oxygen or nitrate as the electron acceptor. The work was conducted as part of a larger experiment designed to assess the potential for biotic or abiotic oxidation of natural and synthetic reduced Fe and S phases in Hanford 300 Area sediments. Neutral-pH chemolithoautotrophic enrichment cultures were amended with synthetic framboidal pyrite and inoculated with sediment from at or below the redox transition in 300A sediments. The synthetic pyrite was washed extensively with 6M HCl and acetone to remove potential FeS and S^0 contaminants. XRD analysis revealed the presence of pyrite with small quantities of marcasite; no other Fe or S phases were detected. This result is consistent with the observed 1:2 Fe:S ratio of the synthetic framboids. SEM analysis revealed that the μm-sized framboids consisted of aggregates of much smaller (5-10 nm) crystallites.

Several aerobic enrichment cultures capable of chemolithoautotrophic oxidation of synthetic framboidal pyrite linked to sulfate generation were recovered. The extent of sulfate generation in the cultures was several-fold higher than in parallel sterile (uninoculated) controls. No significant sulfate generation was observed in cultures with nitrate as the electron acceptor. Activity of the aerobic cultures was sustained through more than 15 successive transfers over 400 days. The amount of sulfate generated indicated 10-20% oxidation of pyrite. The ratio of Fe(II) to total Fe in 0.5M HCl extracts of the solids declined over time, consistent with concomitant Fe and S oxidation. TEM analysis showed thin coatings of amorphous Fe(III) oxyhydroxides on oxidized framboids, and linear combination fit analyses of Fe K-edge EXAFS showed increased concentrations ferrihydrite and decreased FeS_2 concentrations in the oxidized pyrite. No distinct S-bearing mineral phases were detected by SEM, TEM, or XRD. S K-edge XANES confirmed the absence of S in anything other than the -2 oxidation state, consistent with complete oxidation of FeS_2 to sulfate.

DNA-based staining and fluorescence microscopy, cryo-SEM, and Fluoresce In-Situ Hybridization (FISH) showed that microbial cells were intimately associated with the pyrite grains. FISH revealed association of both Alpha- and Betaproteobacterial communities with pyrite grains. The composition of the enrichment cultures was assessed using conventional 16S rRNA gene clone libraries. Consistent with the FISH results, the clone libraries were dominated by Alphaproteobacteria (*Bradyrhizobiaceae*, *Mesorhizobium*) as well as organisms related to the Betaproteobacterial genus *Ralstonia*. A culturing

campaign isolated a novel *Bosea* strain (*Bradyrhizobiaceae*) capable of chemolithoautotrophic growth through thiosulfate oxidation. Assessment of the ability of the thiosulfate-oxidizing *Bosea* strain to oxidize pyrite is underway. This research was supported by the SBR SFA at Pacific Northwest National Laboratory.

NAME: Kevin Rosso
ORGANIZATION: Pacific Northwest National Laboratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Redox Behavior of Hanford 300A Fe-Phyllosilicates, Fe-Oxides and Key Biomolecules

ABSTRACT: This research seeks to understand the oxidation/reduction behavior of important mineralogic forms of Fe in the redox transition zone (RTZ) of the Hanford 300A site, associated mechanisms of electron transfer and linkage to carbon and nitrogen cycling across this zone in the subsurface. Select natural Fe minerals from core samples are being isolated, with a focus on Fe-bearing clay, along with analog phases to probe their redox reactivity in nitrification/denitrification in terms of the site structure, occupancy and valence of lattice Fe. Electron transfer kinetics with key microbial outer-membrane cytochromes are also being examined to understand relevant Fe(II)/Fe(III) biotransformation mechanisms. Combined laboratory experimental and computational molecular simulation approaches at user facilities such as the EMSL and the ALS are being used to gain fundamental insight that is prospectively generalizable to other similar subsurface systems.

RTZ sediments are relatively rich in an Fe-bearing 2:1 smectitic clay consistent with Fe-beidellite, a phase that can act as both an Fe(II)-bearing electron source in reduced form below the transition, and an Fe(III)-bearing electron sink in oxidized form above the transition. These minerals can contain Fe in both octahedral and tetrahedral coordination in variable proportion and absolute concentrations, a compositional and structural characteristic expected to impact the net Fe(II)/Fe(III) redox potential. Fe site-occupancy and valence in RTZ Fe-clay along with NAu-1 and NAu-2 Fe-nontronites for comparison were analyzed in oxidized and reduced forms, naturally and chemically reduced, by synchrotron Fe L-edge x-ray absorption (XA) and magnetic circular dichroism spectroscopies (XMCD). XA/XMCD shows that oxidized forms are dominated by magnetically ordered octahedral Fe(III) with no apparent tetrahedral Fe(III), and with increasing extent of reduction an octahedral Fe(II) component becomes apparent with increasing magnetic ordering consistent with more prominent exchange interaction facilitated by an increasing concentration of Fe(II)-O-Fe(III) groups in the octahedral sheet. Computational molecular simulation of the electron transfer exchange rate between such groups indicate an electron mobility from within the lattice towards redox-reactive and accessible edge sites, and vice versa, on the order of 10^5 electrons per second, suggesting rapid electron exchange with adsorbed redox-active species.

Key outer-membrane multi-heme cytochromes from metal reducing and oxidizing bacteria are being examined for their rate of electron transfer interaction with these important Fe-mineral phases. Molecular simulation of hopping electron transport through the deca-heme cytochrome MtrF indicates a sustainable and reversible overall rate of 5×10^4 electrons per second, near that sustainable by 300A Fe-clay minerals. Rates of Fe(II)/Fe(III) oxide nanoparticle oxidation by the deca-heme cytochrome MtoA, and reduction by the deca-heme cytochrome OmcA, are being measured using UV-visible spectroscopy on the protein, and using in situ x-ray diffraction and XA/XMCD on the nanoparticles, to understand biomolecular and mineralogic controls on interfacial electron transfer efficiency; similar studies with the 300A Fe-clay are planned, including measuring redox rates and affects on aqueous N speciation. This research, part of the PNNL Science Focus Area, will improve understanding of the limits of redox reaction kinetics possible between dominant Fe-mineralogy, groundwater species, and microorganisms interacting with these phases in the RTZ.

NAME: Liang Shi
ORGANIZATION: Pacific Northwest National Laboratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Electron Transfer Mechanisms for Microbial Iron Redox Cycle in Hanford Subsurface Sediments

ABSTRACT: Iron (Fe) is the fourth most abundant element in the earth and present at between 3.5 and 8% (by weight) in the subsurface sediments of Hanford 300 area (300A). It represents a large reservoir of oxidant [i.e., Fe(III)] and reductant [Fe(II)] for microbial energy generation, in which Fe(III) reduction is coupled to oxidation of organic matter and probably methane, while Fe(II) oxidation is coupled to reduction of O_2, nitrate and CO_2. Critical to this Fe(II/III) redox cycling are the microbial electron transfer pathways that physically link the extracellular Fe redox reactions and the intracellular metabolic activities. These electron transfer pathways in the 300A microorganisms are, however, essentially unknown.

Heme-staining analyses of the Fe(III)-reducing bacterium *Geobacter* sp. FA1 (FA1) isolated from the 300A reveals that the abundance of a heme-containing protein, whose apparent molecular mass is close to that of OmcB of the model Fe(III)-reducing bacterium *G. sulfurreducens* PCA (PCA), increases under the Fe(III)-reducing condition. The PCA OmcB is an outer membrane, 12-heme *c*-type cytochrome that resides on the bacterial surface where it is involved in Fe(III) reduction. A gene encoding a putative outer membrane *c*-type cytochrome with multiple hemes was subsequently cloned and sequenced from the FA1 genome. Its deduced amino acid sequence is 38% identical to that of PCA OmcB and possesses 12 heme-binding motifs. This cloned gene is named as *omcB* and its protein product OmcB is hypothesized to be part of extracellular electron transfer pathways used for Fe(III) reduction by FA1. To test this hypothesis, current research focuses on (i) the role of FA1 OmcB in Fe(III) reduction, (ii) purification and characterization of FA1 OmcB and (iii) determination of the whole genomic sequence of FA1 through the JGI Microbial Isolates Sequencing Program.

c-Type cytochromes and multicopper oxidases play important roles in microbial Fe(II) oxidation. Analysis of a drafted whole genomic sequence for the chemolithoautotrophic Fe(II)-oxidizing bacterium *Bradyrhizobium* sp 22, which is also isolated from the 300A, has identified 75 putative *c*-type cytochromes and 6 putative multicopper oxidases. Further analyses have also identified the putative proteins that may be used for nitrate reduction and CO_2 fixation. To investigate whether these identified proteins are involved in Fe(II) oxidation that is coupled to nitrate reduction and CO_2 fixation, development of a genetic system for *Bradyrhizobium* sp 22 has been initiated.

A proteoliposome system is successfully developed to investigate the interfacial electron transfer reactions between the surface-exposed bacterial terminal metal reductases and Fe(III) minerals. Immuno-gold localization and proteolytic digestion consistently demonstrate that the topology of the bacterial reductases on the proteoliposomes is the same to that on the bacterial cells. By providing a continuous flow of electrons, the proteoliposome experiments demonstrate that conduction through the bacterial terminal metal reductases directly to Fe(III) minerals is sufficient to support *in vivo*, anaerobic, solid-phase Fe(III) respiration. This system will be used to characterize electron conductance properties of the pathways identified from the 300A microorganisms.

This research is part of the SBR SFA at Pacific Northwest National Laboratory.

NAME: James Stegen
ORGANIZATION: PNNL
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Quantifying Subsurface Microbial Community Assembly Processes

ABSTRACT: Spatial turnover in the composition of biological communities is governed by (ecological) Drift, Selection, and Dispersal. Commonly applied statistical tools cannot quantitatively estimate these processes, nor identify abiotic features that impose these processes. For interrogation of subsurface microbial communities distributed across two geologically distinct formations of the unconfined aquifer underlying the Hanford Site 300 Area in southeastern Washington State, we developed an analytical framework that advances ecological understanding in two primary ways. First, we quantitatively estimate influences of Drift, Selection, and Dispersal. Second, ecological patterns are used to characterize measured and *unmeasured* abiotic variables that impose Selection or that result in low-levels of Dispersal. We determined that (*i*) Drift alone consistently governs ~25% of spatial turnover in community composition; (*ii*) in deeper, finer-grained sediments Selection is strong (governing ~60% of turnover), being imposed by an unmeasured, but spatially structured environmental variable; (*iii*) in shallower, coarser-grained sediments Selection is weaker (governing ~30% of turnover), being imposed by vertically and horizontally structured hydrologic factors; (*iv*) low-levels of Dispersal can govern nearly 30% of turnover and be caused primarily by spatial isolation resulting from limited exchange between finer and coarser-grain sediments; and (*v*) highly permeable sediments are associated with high-levels of Dispersal that homogenize community composition and govern over 20% of turnover. This framework provides inferences that cannot be achieved using pre-existing approaches, and suggests that their broad application will facilitate a unified understanding of microbial communities. These approaches are being applied to molecular analyses of microbial communities in the Hanford 300A subsurface and Columbia River hyporheic zone to assess system-scale ecological impacts of river water intrusion into the subsurface during the spring runoff.

NAME: John Zachara
ORGANIZATION: Pacific Northwest National Laboratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Biogeochemical Investigations Across Oxidation-Reduction Boundaries at the Hanford Site SFA

ABSTRACT: The area near the Columbia River shore at the 300 Area comprises a complex system where microbial populations and associated activities are controlled by processes occurring across lithologic boundaries where contrasting nutrient availability and transport properties impose transitions in oxidation-reduction potential. While the regional hydrologic gradient is generally from surrounding uplands toward the Columbia River, seasonal and short-term changes in river stage cause fluctuations in the gradient such that the groundwater flow direction and velocity, and water table elevation are highly variable. Our focus here is on C, N, and elemental biogeochemical cycles across the contact zone between young (~15,000 years), highly-transmissive Hanford formation sediments; and older (~3.5 My), finer-grained Ringold Formation sediments that lie immediately below.

A series of passive multilevel samplers were deployed across known fine-to-coarse lithologic boundaries at the top and bottom of the Ringold Formation's uppermost mud. Deployment locations included two IFRC wells and three others in the extended 300 A monitoring network. Aqueous and dissolved gas samples were analyzed for the metabolically sensitive solutes O_2, NO_3^-, NO_2^-, SO_4^{2-}, Mn^{2+}, Fe^{2+}, HS^-, H_2, and CH_4. Sediment samples from above, within, and below the contact zone were analyzed for carbon forms, sulfur species, iron valence, mineralogy [including Fe(II) phases], pore scale physical features by x-ray tomography, and microbial community structure and function as determined by q-PCR assays and 16S gene sequencing.

Across the gravel-mud boundary from the Hanford to Ringold formations, the concentrations of SO_4^{2-}, Mn^{2+}, HS^-, NO_2^-, H_2, and CH_4 increased with depth, while the concentrations of O_2 and NO_3^- decreased. Dissolved ferrous iron and Mn^{2+} were present throughout the sampled Ringold formation. Mineralogic and chemical analyses revealed the presence of an abrupt redox transition zone (rtz) within the Ringold mud. Iron within ubiquitous phyllosilicates above the rtz was in the oxidized form, while Fe in deeper phyllosilicates was reduced and framboidal pyrite was present. Anaerobic metabolism, heterogeneously distributed within the fine portions of the Ringold formation, was catalyzed by relatively small but active microbial populations that consumed dissolved and solid-phase electron acceptors including nitrate, Fe(III), and sulfate. H_2 and CH_4 concentration gradients suggested that slow fermentation of detrital organic matter supplied electron donor that drove sequential electron donor consumption across the lithologic boundary. Concentration gradients imply transport from the Ringold to the Hanford formation that are likely responsible for system-scale maintenance of redox boundaries in the greater 300.

SUBSURFACE BIOGEOCHEMICAL RESEARCH

SLAC SCIENTIFIC FOCUS AREAS (SFA)

NAME: John Bargar
ORGANIZATION: SLAC National Accelerator Laboratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: SLAC SFA: Molecular-scale biogeochemical controls over uranium, sulfur, and iron redox cycling in the subsurface

ABSTRACT: Recent field studies show that both uraninite and non-crystalline U(IV) are produced following biological metal and sulfate reduction of aquifers containing uranium. This objective of this work was to develop enhanced molecular-scale understanding of the biogeochemical factors controlling the formation and stability of these species in the subsurface. The chemical conditions present during bioreduction were systematically examined to identify specific groundwater solutes favoring the formation of non-crystalline U(IV). Sulfate and silicate were found to promote the formation of the non-crystalline U(IV) product while others such as calcium, magnesium and sodium did not. Phosphate also promotes non-crystalline U(IV) formation. Additionally, the formation of this product was linked to the biological response of *Shewanella oneidensis* MR-1 cells to U(VI). In the presence of these solutes, cells produced abundant exopolymeric substances (EPS). Scanning transmission X-ray microscopy (STXM) revealed that U was co-localized with EPS when non-crystalline U(IV) was produced and with the cell surface when UO_2 was produced. Cell viability assays showed that cells producing EPS were more viable than those producing UO_2.

The biogeochemical redox cycling of S and Fe and its impact on U(IV) speciation and stability in field-biostimulated Rifle, CO IFRC aquifer sediments was evaluated using X-ray absorption spectroscopy, X-ray microscopy, electron microscopy, and chemical extractions. These findings show that zero-valent sulfur is relatively abundant prior to and during sulfate reduction. The onset of microbial sulfate reduction corresponds with the formation of FeS coatings and a sharp escalation of U(IV) accumulation rates. Intriguingly, U(IV) speciation is not appreciably impacted by the onset and intensity of sulfate reduction, suggesting that bacteria play direct and profound roles in stabilizing U(IV) under all conditions examined.

Further, we characterized the reactivity of crystalline and non-crystalline U(IV) products by exposing chemogenic UO_2, biogenic UO_2 or non-crystalline U(IV) to various complexants and oxidants and then evaluating the release of U as well as changes in solid-phase speciation. Reactivity assay reagents included ammonium nitrate and fluoride under anoxic conditions and dissolved oxygen and persulfate as oxidants. The results show that non-crystalline U(IV) is more readily mobilized by complexation either form of UO_2, and that persulfate is a potent oxidizer of all forms of U(IV). U L_{III} edge x-ray absorption spectroscopy confirmed that non-crystalline U(IV) was more susceptible to rapid oxidation than UO_2.

This work provides detailed new process models and quantitative parameters that inform biogeochemical models of uranium redox transitions in aquifers.

NAME: John Bargar
ORGANIZATION: SLAC National Accelerator Laboratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: SLAC SFA: Biogeochemical controls over C, S, Fe, and U redox cycling in NOM-rich naturally reduced aquifer sediments

ABSTRACT: Work by the DOE-BER Rifle IFRC has identified zones of organic-rich reduced sediments at the Old Rifle, CO uranium ore processing site. These naturally reduced zones (NRZs) contain more than 100-fold higher U than ambient sediments and are suspected to play significant roles in maintaining the persistent uranium groundwater plume at this site. The similarity of Old Rifle to other uranium-contaminated alluvial aquifers, coupled with observations of naturally reduced uranium at other sites, suggests that NRZs may be 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. These deeply buried NOM-rich zones also provide information on carbon cycling and sequestration processes associated with export of litter-derived organic carbon to the subsurface.

The SLAC SFA program is performing work to elucidate the biogeochemical processes governing the formation, reactivity, and oxidation of the biogeochemically active elements C, S, and Fe within NRZs. Process-based mechanistic models will be developed to understand the fate of uranium and carbon within NRZs. Key questions that we seek to investigate are: what is the spatial extent of the NRZs in the aquifer? How does the speciation of C, S, Fe, and U vary spatially within the NRZs? How do C, S, and Fe within NRZs undergo transform upon oxygenation during annual and long-term de-saturation, and how do these transformations impact U oxidation? What is the role of NOM as a complexing and reducing agent for U(VI)? We are presently characterizing NRZ sediments from the Old Rifle site and conducting a series of diffusion-limited NOM-amended experiments to simulate the formation of NRZs. We have observed a spatial distribution of uranium retention processes across redox gradients created by simulated NRZs, with U(VI) adsorption transpiring in the external regions, progressing through U(V) incorporation into goethite, and developing uraninite within the interiors of the NRZs. Further, we note that Fe(II) concentrations have the primary role in dictating the specific retention process of uranium within these systems. Subsequent to our investigation of NRZ formation within simulated environments, we will explore their oxidation. We are using a combination of approaches to characterize the distribution and speciation of C, S, Fe, and U in these materials and experiments, including x-ray absorption spectroscopy, micron-scale x-ray microprobe elemental and mineral-specific imaging, and scanning transmission x-ray microscopy (STXM) and nano-SIMS. 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.

SUBSURFACE BIOGEOCHEMICAL RESEARCH

UNIVERSITY-LED RESEARCH

NAME: Estella Atekwana
ORGANIZATION: Oklahoma State University
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Induced Polarization Signature of Biofilms in Porous Media: From Laboratory Experiments to Theoretical Developments and Validation

ABSTRACT: There is a need for appropriate techniques that can monitor the growth of microbial communities *in situ* and the coupled biogeochemical and biogeophysical processes. Spectral Induced Polarization (SIP), a biogeophysical technique, can play a key role. However, the triggering mechanisms of SIP responses modulation by biogeochemical activity of microbial communities (biofilm) remain poorly understood. The overarching goal of this project is to find the correlations between biogeochemical processes occurring within subsurface microbial communities and spectral induced polarization (SIP) signatures in aqueous and/or porous media. *Anticipated findings will allow for the interpretation of the geophysical responses associated with the development of microbial communities in field conditions.*

We investigated the SIP response of biofilm components including cells, exopolysaccharides (EPS), cells in EPS and semi-conductive particulate matter such as magnetite in EPS. Using microbial cells from three different model organisms in liquid suspension and in porous media, we observed an increase in SIP parameters with increasing cell density with a very well defined relaxation peak at a frequency of ~10 Hz which was predicted by recently developed quantitative models. However this characteristic relaxation peak was minimized in the presence of porous media. We also observed that cells suspended in EPS enhances the polarization and also shows a peak frequency at ~10 Hz.

The study of alginate gelation (representing EPS) in liquid phase and porous media *in vitro* revealed that solidified (gelated) alginate isolated from brown algae increased the magnitude of imaginary conductivity while real conductivity increased very moderately. In contrast, the study of the SIP response within a porous medium filled with solidified gel of alginate isolated from mucoid strain *P. aeruginosa* FRD-1 showed an increase in the magnitude of both imaginary and real conductivities. Further, the addition of magnetite particulates in the EPS enhanced the gelation process and the magnitude of the SIP response.

We also continued with the development of our quantitative model to investigate frequency-domain induced polarization response of suspensions of bacteria and bacteria growth in porous media. Our model results show that the growth rate and endogenous decay coefficients of bacteria in porous sand can be inferred non-intrusively from time-lapse frequency-domain induced polarization data.

Conclusions: 1) the time-lapse SIP data are applicable for the evaluation of growth rate and endogenous decay of bacteria in porous media. This finding helps to enhance the interpretation of SIP measurements from field sites; 2) SIP parameters are sensitive to the transition of an alginate from liquid to solidified stage;3) the magnitude of SIP signatures reflects both cell density, biofilm maturity and the presence of secondary minerals; and 4) bacteria may have a characteristic low frequency relaxation peak at 10 Hz..

Our next goals include but not limited to the study of the modulation of SIP responses by field-relevant organisms *Geobacter sulfurreducens* along with its ΔpilA mutant, and *Disulfovibrio vulgaris*. Anticipated results will be useful for the development of a mechanistic model for the induced polarization response.

NAME: Jill Banfield
ORGANIZATION: University California Berkeley
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Genome-enabled analysis of subsurface microbial communities and their response to acetate stimulation

ABSTRACT: The subsurface is a massive reservoir of carbon compounds and hosts a large fraction of the microbial life on earth. Despite this, relatively little is known about sediment communities and their roles in carbon, nitrogen, and hydrogen cycling in the subsurface. We metagenomically sequenced unstimulated (background) sediment samples, as well as acetate stimulated sediment and planktonic communities from Rifle, CO to document microbial composition and metabolic potential. Background aquifer sediments are highly diverse; no single organism constitutes more than 1% of the community. Many of the lineages in sediment are novel, at least fifteen at the phylum level. We reconstructed a complete genome from the dominant background sediment organism, RBG-1, a representative of a previously undescribed bacterial phylum. This organism is metabolically versatile, with a large complement of respiratory machinery that likely enables dominance in sediments subjected to fluctuating redox conditions. Chloroflexi are surprisingly diverse and relatively abundant in background sediments. We reconstructed draft genomes for genomically unsampled members of the Chloroflexi, some of which are capable of carbon fixation and other biogeochemical processes. Archaea are also relatively abundant in background sediment. Among the archaea genomically characterized, we recovered a few Thaumarchaeaota, and a vast clade of novel Halobacteriales.

We documented very different sediment-associated and planktonic communities, both with and without acetate amendment. From acetate-stimulated sediment, we recovered nearly 100 high quality complete and draft genomes and reconstructed organism abundance patterns within the geochemical context. The results indicate the importance of Bacteroidetes, Betaproteobacteria, and bacteria from phyla lacking (e.g., SR1, OP11, OD1, WWE3) or with very few (e.g., Ignavibacteria, Elusimicrobia) cultivated representatives. Metagenomic sequencing of acetate-stimulated groundwater filtered through a 0.2 µm filter revealed the predominance of bacteria from OP11, OD1, and WWE3 on the 0.1 µm filter. Cryo-TEM characterization demonstrated cell sizes below the theoretical minimum size for life. We also reconstructed over 1,000 complete phage genomes. In a majority of cases phage can be linked to their hosts via CRISPR spacer targeting. The planktonic community composition shifts during the biostimulation process. Notably, genomes were reconstructed for TM6 lineage bacteria from samples on the 0.2 µm filter were collected only late in biostimulation. From the same experiment, methanogens were notable by their near-absence, despite evidence for methane production.

NAME: Tamar Barkay
ORGANIZATION: Rutgers University
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Oxidation of Hg(0) to Hg(II) by Anaerobic Bacteria: Its Effect on Hg Stable Isotope Fractionation and Methylmercury Production

ABSTRACT: **Background:** The methylation of inorganic Hg is known to be mediated by microorganisms under anoxic conditions. Previous studies have elucidated the chemical species of mercuric Hg [Hg(II)] that are bioavailable to methylating microbes. The reduced form of mercury, elemental Hg [Hg(0)], is generally considered chemically inert and unavailable for biologic uptake by anaerobic bacteria. However, the oxidation and subsequent methylation of Hg(0) by anaerobic bacteria have never been tested. In this project, we are conducting laboratory experiments to examine the anaerobic oxidation of Hg(0) and the effect of microbial Hg(0) oxidation on Hg stable isotope fractionation and MeHg production.

Hypotheses:
1: In anoxic environments, anaerobic bacteria catalyze the oxidization of Hg(0) to Hg(II).
2: Microbial oxidation of Hg(0) to Hg(II) imparts a mass-dependent fractionation of Hg stable isotopes.
3: Anaerobic Hg-methylating bacteria produce MeHg when provided with Hg(0) as the sole Hg source.

Results: We examined the Hg(0) oxidation activity of the obligate anaerobic bacteria *Desulfovibrio desulfuricans* ND132 (Deltaproteobacterium) and *Geothrix fermentans* H5 (Acidobacterium), and the facultative anaerobic bacteria *Shewanella oneidensis* MR-1 (Gammaproteobacterium) and *Ralstonia metallidurans* AE104 (Betaproteobacterium). Anoxic cultures were exposed to Hg(0) in the dark, and samples were collected and analyzed for the formation of non-purgeable Hg. We found that all four bacterial strains produced non-purgeable Hg from dissolved Hg(0) under anoxic conditions. Derivatization of the non-purgeable Hg in the cell suspensions to diethylmercury and analysis of Hg(0)-reacted bacterial cells using X-ray absorption near edge structure (XANES) spectroscopy demonstrated that cell-associated Hg was dominantly in the oxidized Hg(II) form.

The fractionation of Hg stable isotopes by microbial Hg(0) oxidation was investigated using multi-collector inductively coupled mass spectrometry. Oxidation of Hg(0) to Hg(II) by *D. desulfuricans* ND132 resulted in mass-dependent fractionation of Hg stable isotopes.

The production of methylmercury by *D. desulfuricans* ND132 was determined by distillation and ethylation-gas chromatography. When exposed to a constant source of Hg(0), *D. desulfuricans* ND132 produced up to 118 µg/L of methylmercury after 36 h of incubation. A major fraction of the methylated Hg was exported out of the cell and released into the culture medium. These results indicate that anaerobic Hg-methylating bacteria can catalyze the oxidization of Hg(0) to Hg(II), and produce MeHg when provided with Hg(0) as the sole Hg source.

NAME: Joel Blum
ORGANIZATION: University of Michigan
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Isotopic Characterization of Biogeochemical Pools of Mercury and Determination of Reaction Pathways for Mercury Methylation

ABSTRACT: This project utilizes stable Hg isotopes to reveal locations of Hg methylation in the East Fork Poplar Creek (EFPC) watershed, TN and to place constraints on processes that lead to methylmercury (MeHg) production, transport and degradation. During the first 16 months of the project we: 1) completed three sampling campaigns (fall, spring, and summer) in which water, sediment, and periphyton from EFPC, Hinds Creek and adjacent wetlands were collected, 2) developed protocols and collected samples of dissolved gaseous mercury (DGM) from EFPC stream water, 3) obtained samples of fish tissues from the ORNL Ecological Assessment Group, 4) obtained samples of Clinch River and EFPC sediments from TN Dept. of Environ and Conservation, 5) completed Hg and MeHg concentration analyses and Hg isotopic analyses of sediments, suspended particulates, surface waters, pore waters, and periphyton from one entire field sampling campaign, as well as fish tissues, and 6) conducted photochemical and dark oxidation experiments with EFPC water and model ligands to investigate Hg isotope fractionation.

Sediments downstream of Y-12 in EFPC had elevated THg concentrations (3.2 to 60 ug/g) compared to background sediments, and average δ^{202}Hg of 0.11 ± 0.11‰ and Δ^{199}Hg of -0.08 ± 0.03‰ (mean ± 1s.d.; n=6). The THg concentration of sediments downstream in Poplar Creek (PC) and the Clinch River remains elevated (0.24 to 3.9 ug/g) and δ^{202}Hg has a range between -0.82‰ and 0.07‰. Sediments in the Clinch River and Hinds Creek upstream of the confluence with PC have THg concentrations between 0.01 and 0.05 ug/g and the Hg isotopic composition is distinct from downstream sites (δ^{202}Hg of -1.40 ± 0.06‰ and Δ^{199}Hg of -0.25 ± 0.03‰). The results demonstrate that Y-12 impacted sediments have a unique Hg isotopic composition that persists in EFPC and can be traced downstream to PC and the Clinch River.

Mercury isotopic composition within the EFPC stream corridor changes with distance from the Y-12 complex to its confluence with PC. Stream water concentrations of dissolved total mercury (THg_d) decreased from 66 ng/L at Station 8 within the Y-12 complex, to 17 ng/L near the confluence with PC, δ^{202}Hg decreased from -0.11‰ to -0.19‰, and Δ^{199}Hg decreased from 0.06‰ to -0.06‰. Isotopic composition of suspended sediment also shifts from the Y-12 complex (δ^{202}Hg = -0.60‰, Δ^{199}Hg = 0.02) to downstream reaches (δ^{202}Hg = 0.07‰, Δ^{199}Hg = -0.12‰). The isotopic composition of DGM ranged from δ^{202}Hg values of 0.97‰ to 1.10‰ and Δ^{199}Hg values of -1.52‰ to -0.29‰, differing significantly from that of stream water, suspended particulate matter, and sediments. Changes in mercury concentration and isotopic composition along the flow path within the EFPC can be interpreted within the context of isotopic data from laboratory Hg(0) photochemical and dark oxidation experiments.

We used fish mercury isotope composition and %MeHg to estimate the isotopic composition of the sources of inorganic Hg (IHg) and MeHg accumulating in fish. In the heavily IHg contaminated EFPC, we estimated

NAME: Bill Burgos
ORGANIZATION: Penn State University
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Reactivity of Iron-Bearing Phyllosilicates with Uranium and Chromium Through Redox Transition Zones

ABSTRACT: Hexavalent chromium (Cr^{6+}) is a major contaminant in the environment. As a redox-sensitive element, the fate and toxicity of chromium is controlled by reduction-oxidation (redox) reactions. Previous research has demonstrated the ability of chemically reduced smectite and aqueous Fe^{2+} to reduce Cr^{6+} to Cr(III) as a way of immobilization under natural conditions. However, it is still poorly known whether or not natural or biologically reduced clay minerals exhibit similar reactivity and if so, what are the kinetics and mechanisms of Cr^{6+} reduction by clay-Fe(II). The objective of this study was to determine the kinetics of Cr^{6+} reduction by Fe(II) associated with various common clay minerals and the nature of reduced Cr(III). The reactivity of clay minerals nontronite (NAu-2), montmorillonite (Swy-2), chlorite (CCa-2), and clay-rich sediments from the Ringold Formation of the Hanford site of Washington State towards reduction of Cr^{6+} was studied. Structural Fe(III) in the clay minerals was first bioreduced to Fe(II) by *Geobacter sulfurreducens* with acetate as the sole electron donor and anthraquinone-2,6-disulfate (AQDS) as electron shuttle in select experiments in synthetic groundwater (pH-7). Biogenic Fe(II) was then used to reduce Cr^{6+} at three different temperatures, 10°, 20° and 30°C, in order to determine the activation energy of the redox reaction between Cr^{6+} and clay-Fe(II). The results showed that nontronite was the most effective in reducing Cr^{6+} at all temperatures and chlorite the least. Despite a large amount of Fe(III) bioreduction in chlorite, most bio-produced Fe(II) was not reactive towards Cr^{6+} reduction at 10°C, however at 30°C there was some reduction, which was likely due to released Fe^{2+} from the dissolution of chlorite. For all the clay minerals, the ratio of Fe(II) oxidized to Cr^{6+} reduced was close to the expected stoichiometric value of 3 ± 0.5. Scanning electron microscopy with focused ion beam and transmission electron microscopy with electron energy loss spectroscopy (TEM-EELS) characterization revealed that reduced chromium was Cr(III) and it was closely associated with residual nontronite NAu-2 as micron-scale aggregates. This unique textural association was expected to minimize any chance of Cr(III) reoxidation upon exposure to oxidants. These kinetic results are important for our understanding of how various clay minerals may be used to reductively immobilize heavy metal contaminants such as Cr, Tc, or U from the environment.

We have also been studying the reactivity of clay-Fe(III) towards the oxidation of uraninite. These experiments have focused on the comparing the reactivity of biogenic clay-Fe(II) versus chemically reduced clay-Fe(II). Results obtained with nontronite NAu-2 suggest that only 25 to 35% of the structural clay-Fe(III) can be reduced by a variety of oxidants (including DMRB, quinones, and uraninite). Experiments are now being conducted with nontronite NAu-2, DMRB and nitroaromatic compounds (NACs) to operationally define this thermodynamic endpoint.

NAME: Peter Burns
ORGANIZATION: University of Notre Dame
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Inorganic Geochemical Controls on Neptunium Transport: Co-Precipitation in Minerals

ABSTRACT: 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 from 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 about a dozen mineral phases that present different cation sites that are incorporation targets. 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 and quantum mechanical models to bear on the study of the local environments of incorporation.

NAME: Elizabeth Butler
ORGANIZATION: University of Oklahoma
PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Stability of Iron-Chromium Precipitates for Long Term In-Situ Chromium Immobilization

ABSTRACT: The objective of this research was to identify factors affecting the properties of Fe-Cr precipitates formed in microbial and abiotic anoxic systems. Specific objectives were to: (1) measure the rates of Cr(VI) reduction by Fe(II) minerals and microorganisms; (2) characterize the morphology, crystallinity, and composition of the formed Fe-Cr precipitates; and (3) measure oxidation rates of dissolved Cr(III) in equilibrium with these precipitates by birnessite.

Microbially-active microcosms contained hematite, aluminum substituted goethite (Al-goethite), or iron rich nontronite (NAu-2), and *Desulfovibrio vulgaris* strain RCH1 (Chakraborty R., http://www.ncbi.nlm.nih.gov/nuccore/CP002297.1) (RCH1). Microcosms containing hematite were prepared with a low and high dilution of the culture to yield faster (hematite/RCH1/fast) or slower (hematite/RCH1/slow) Cr(VI) removal. Abiotic microcosms contained either FeS or dithionite reduced NAu-2. Dissolved Cr(VI) was removed relatively rapidly in all microcosms, with the fastest Cr(VI) disappearance for FeS (30 minutes), and the slowest for hematite/RCH1/slow (one month). Thus, in all systems, Cr(VI) was removed from solution in the time scale of ground water transport.

After the kinetic experiments, the solids were retrieved, washed, and dried. X-ray absorption spectra indicated the presence of mixed Fe(III)-Cr(III) hydroxide phases for all solids. Although the majority of solid phase Cr was in the +III oxidation state, solid phase Cr(VI) was also identified at a relative concentration of 21-25% for RCH1/hematite (slow and fast) and RCH1/Al-goethite, 10-11% for RCH1/NAu-2 and dithionite reduced NAu-2, and 4% for FeS. Transmission electron microscopy (TEM) and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) were done to further characterize the solids. The most pronounced morphological changes after reacting with Cr(VI) were observed for RCH1/hematite/fast and FeS. TEM images of RCH1/hematite/fast after reaction with Cr(VI) show jagged edges and pitting, as well as development of a very thin surface layer, suggesting dissolution of hematite and formation of a new phase. TEM and SEM images showed a possible organic film in which nanoparticles with the highest Cr:Fe ratio (approximately 1) were observed. TEM analysis of FeS after reacting with Cr(VI) indicated a poorly crystalline, essentially amorphous material with individual grains difficult to distinguish at the nanoscale. SEM/EDS of this material showed elevated Cr, increased O, and decreased S, suggesting formation of a Cr-Fe hydroxide.

Finally, each solid was equilibrated in the presence of an aqueous suspension of birnessite (along with controls containing no birnessite) for approximately two weeks. We speculated that dissolved Cr(III) in equilibrium with each Fe-Cr solid might be oxidized by the birnessite to Cr(VI), driving further Cr(III) dissolution and oxidation. Solid phase Cr(VI), present at significant quantities in some solids, could also dissolve, regardless of whether birnessite was present. All solids from the microbially-active microcosms showed only minimal release of Cr(VI), and no significant difference in dissolved Cr(VI) concentration in the presence of birnessite compared to the control. FeS and dithionite-reduced NAu-2, on the other hand, showed a steady increase in concentration of Cr(VI) over time, suggesting that these precipitates may be susceptible to re-mobilization of Cr in the subsurface.

NAME: Andres Campiglia

ORGANIZATION: Department of Chemistry, University of Central Florida

PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Field-Deployable Nanosensing Approach for Real-time Detection of Free Mercury

ABSTRACT: Our proposition targets a critical element of the Environmental Remediation Science Program (ERSP) research portfolio, which is the development of enabling scientific tools for characterizing the spatial and temporal evolution of complex subsurface systems. We propose a field-portable, on-site sensing device for real-time speciation of elemental and inorganic mercury in surface stream waters, groundwater, and sediment samples. During the past year of the project, our efforts were directed towards: (a) the development of an optically transparent nanorod-modfied electrode for measurement of mercury using surface plasmon resonance (SPR) with electrochemical reduction of Hg species; and (b) the design and set-up of a portable spectrometer (prototype) for field measurements of mercury. A systematic approach was developed for the immobilization of gold nanorods (Au NR) on Indium Tin Oxide (ITO)-coated glass cover slides via covalent binding through (3-mercaptopropyl)trimethoxysilane (MPTMS). Experimental parameters were optimized for appropriate MPTMS surface coverage, CTAB removal, and ionic strength conditions that provide reproducible immobilization of commercially-available Au NRs on ITO surfaces. An application of potential controlled SPR sensing is demonstrated with Hg-Au amalgam formation at the NR surface, where $HgCl_2$ is reduced with applied potential at the Au NR surface, resulting in a characteristic change in SPR spectrum. The original version of the portable spectrometer was significantly improved with the implementation of numerous modifications. These included newly designed sensor head (or sensor box) and input box for fiber optic bundles. Instrument control is now possible with the aid of a laptop. An in-house LabView data acquisition program facilitates computer control of the water flow, real-time spectral acquisition, correlation of maximum wavelength shifts to mercury concentration and instrument calibration.

NAME: Jeffrey Catalano
ORGANIZATION: Washington University in St. Louis
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Dominant Mechanisms of Uranium-Phosphate Reactions in Subsurface Sediments

ABSTRACT: Phosphate addition is an in situ remediation approach being considered by the DOE 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 in treated systems. 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 identify the U(VI)-phosphate precipitates that form from homogeneous solutions, characterize the cooperative and competitive effects of phosphate on U(VI) adsorption and precipitation on smectite and iron oxide minerals, and then investigate how phosphate affects U(VI) speciation and fate in sediments from the Rifle and Hanford sites.

Batch experiments were performed to determine the products of U(VI)-phosphate precipitation in homogeneous systems and the resulting equilibrium solubility of those solids as a function of groundwater composition. In the absence of groundwater cations (e.g., Na^+ and Ca^{2+}) metastable chernikovite [$H_3O(UO_2)(PO_4)\cdot 3H_2O$] forms instead of the thermodynamically stable uranyl orthophosphate [$(UO_2)_3(PO_4)_2\cdot 4H_2O$]. Sodium and calcium addition affect U(VI)-phosphate precipitation, with the former inducing the precipitation of Na-autunite [$Na(UO_2)(PO_4)\cdot 3H_2O$] whereas calcium causes U(VI) removal through both autunite [$Ca(UO_2)_2(PO_4)_2\cdot 11H_2O$] precipitation and adsorption onto or incorporation into calcium phosphates.

Separate batch experiments have been conducted to investigate how phosphate affects U(VI) adsorption and precipitation in the presence of montmorillonite and goethite. For both systems, supersaturation is required before the nucleation and precipitation of Na-autunite initiates. The critical supersaturation needed for Na-autunite precipitation on goethite was twice that for montmorillonite. Before the onset of precipitation, U(VI) binding is through adsorption processes. Phosphate has a negligible effect on macroscopic U(VI) adsorption to montmorillonite at pH 4, 6, and 8 despite evidence from EXAFS and TRLFS spectroscopies for ternary complexation. In contrast, phosphate enhances U(VI) adsorption to goethite at pH 4 but suppresses adsorption at pH 8; the former is attributed to U(VI)-phosphate ternary complexation and the latter to surface site competition between U(VI) and phosphate.

Our efforts are currently transitioning to batch and column studies of U(VI)-phosphate reactions in sediments from the Rifle site in Colorado. Batch studies in artificial Rifle groundwater show negligible U(VI) sorption except above 10^{-5} M initial U(VI). The addition of phosphate reduces U(VI) sorption. Studies of U(VI) speciation and the origin of this inhibitory effect are ongoing. Column experiments have also been initiated to examine the influence of phosphate on U(VI) transport, again in artificial groundwater. Following uranium loading, half of the columns then received artificial groundwater amended with phosphate and the other half received phosphate-free solutions. Flow rates were set to provide environmentally relevant seepage velocities. Periodic stopped flow events are being performed

to assess the effects of intraparticle diffusive transport on overall U(VI) mobility. After reaction, columns will be sampled along their length and characterized to determine U speciation and micro-scale spatial distribution. Similar studies are planned for sediments from the Hanford site.

NAME: Clara Chan
ORGANIZATION: University of Delaware
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Fe-oxidizing microorganisms in microscopic model aquifer systems: toward understanding post-biostimulation permeability reduction and oxidative processes at the Rifle IFRC site

ABSTRACT: At the Rifle IFRC, injection of organic carbon stimulates the production of reduced Fe and S chemical species and also results in significant permeability decreases especially within injection wells. Due to the increase in reduced iron species, we predict that iron oxidizing microbes will further contribute to the decrease in permeability during the reoxidation of the aquifer. We first sought to verify the presence of iron oxidizing microbes in the aquifer through culture based methods. Iron sulfide gradient tube cultures inoculated with Rifle groundwater yielded two isolate strains that oxidize Fe and precipitate iron oxyhyroxides. Neither isolate was related to previously identified iron oxidizing microbes. Isolate CD03 is 98% similar to *Curvibacter delicatus*, and P101 #2 is 97% similar to *Hydrogenophaga taeniospiralis*. The isolates are not obligate iron oxidizers, but are also capable of growth on organic substrates and hydrogen. The diversity of metabolisms allow these organisms to adapt to changing geochemical conditions. Next, we designed a flow through culture chamber that allows for imaging of sediment pore space with multiphoton confocal microscopy. Our goal is to visualize the distribution of cells and biominerals in relation to the pore structure, to gain insight into Fe oxidizer controls on aquifer permeability reduction. We packed the chamber with Nafion, an optically transparent polymer which allows us to image pore spaces. Rifle isolates were inoculated into the simulated aquifer system, then growth media was injected at a constant flow rate. We will present our results demonstrating the distribution of cells and biominerals in pores/pore throats and resulting changes in pore scale architecture.

NAME: Jon Chorover
ORGANIZATION: University of Arizona
PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Uranium and strontium fate in waste-weathered sediments: Scaling of molecular processes to predict reactive transport

ABSTRACT: Multi-faceted lines of inquiry are needed to bridge between molecular- and field-scale information. By focusing them on a common experimental design, we seek to reveal non-linear and emergent behavior in contaminated weathering systems. Silicate weathering reactions in acidic uranium waste streams are expected to result in ripening and aging of waste-containing secondary products.
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) Uranium speciation in legacy sediments from the U-8 and U-12 Crib sites can be reproduced in bench-scale weathering experiments conducted on unimpacted Hanford sediments; (2) 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; (3) Although field contamination and laboratory experiments differ in their diagenetic time scales (decades for field vs. months to years for lab), sediment 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: Geochemical transformations and transport behaviors that occur in bench-scale studies of waste-sediment interaction will eventually be compared with parallel solid-phase analyses of core sample extractions from the acid uranium waste impacted U-8 and U-12 Cribs at Hanford. Crib waste aqueous simulants are being reacted with Hanford sediments in batch and column systems. Coupling of contaminant uptake to mineral weathering is being monitored using a suite of methods both during waste-sediment interaction, and after, when waste-weathered sediments are subjected to infusion with circumneutral background pore water solutions.
Results: We have accomplished a set of one year bench-scale batch weathering and flow-through column experiments where Hanford Sediment was reacted with U-bearing synthetic crib waste (SCW) solutions as a function of pH, U and phosphate concentrations. PO_4 exerts strong control over U speciation at all pH with the rapid precipitation of meta-ankoleite [$K(UO_2PO_4)\cdot 3H_2O$] leading to near complete immobilization of U. Bolwoodite [$K(UO_2)(HSiO_4)\cdot 3H_2O$] increased even in PO_4-containing systems. Without PO_4, U speciation was controlled by the (pH-dependent) rate of silicate weathering. In this case, U immobilization was limited to 25-50% as precipitated becquerelite [$Ca(UO_2)_6O_4(OH)_6\cdot 3H_2O$] or compreignacite [$K_2(UO_2)_6O_4(OH)_6\cdot 3H_2O$] and bolwoodite. Mineral precipitate composition depends on initial solution pH. Carbonate dissolution buffers influent pH 3 solutions to ca. pH 7-8 and initial pH 2 solutions to ca. pH 3-4, with subsequent silicate weathering that makes Si^{4+} available for boltwoodite precipitation. Parallel homogeneous nucleation experiments and thermodynamic calculations

conducted to assess precipitation of reference uranium-bearing phases from supersaturated aqueous solutions confirmed the strong phosphate control over U speciation and multi-speciation of U in its absence. Geochemical modeling was further conducted to assess aqueous speciation and solubility envelopes of U-bearing solids as a function of system composition. These data streams guide follow-on desorption experiments and reactive transport modeling to understand the fate and transport of U in the Hanford subsurface.

NAME: Gary Curtis
ORGANIZATION: U.S. Geological Survey
PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Upscaling of U(VI) Desorption and Transport from Decimeter-Scale Heterogeneity to Plume-Scale Modeling

ABSTRACT: Modeling reactive transport of contaminants in groundwater is uncertain because detailed experimental laboratory data are available at the centimeter scale but field-scale transport occurs on the kilometer scale. In this project we test approaches for incorporating small-scale information into field-scale simulations using extensive datasets collected at bench-, decimeter, and tracer test scales of U(VI) at the Naturita, Colorado UMTRA site.

Laboratory batch experiments using contaminated sediments from the Naturita site indicated that U(VI) desorption was rate-limited and required on the order of 30 days to reach equilibrium. Simulations using a dual domain mass transfer model indicated that after approximately 2 weeks the temporal changes of the U(VI) concentration were driven by weathering reactions. The decimeter scale experiments were conducted in 2.5m long 2D tanks packed with two size fractions excavated from the field site. Desorption of U(VI) was simulated using an equilibrium surface complexation model calibrated to batch data and mass transfer rate parameters estimated by model calibration. Reactive transport in the more permeable fraction was limited by the desorption rate whereas equilibrium was closely approximated in the less permeable material. These results were extended in synthetic upscaling experiments where a 2D domain was successfully simulated by a 1D dual domain model using immobile porosity values estimated from the volume fraction of the less permeable facies.

Analysis and modeling of two tracer tests conducted at the Naturita field site has further demonstrated importance of rate-limited mass-transfer on U(VI) transport. Electrical resistivity measurements used to monitor a tracer experiment that had a high sodium chloride concentration demonstrated that effective parameters for mobile-immobile zone transfer could be determined both along the flowpath as well as locally at an observation well, providing insight into the spatial variability of the mass transfer processes. Results from these studies were extended to simulate U(VI) transport observed in the second tracer test where a low electrical conductivity, U(VI) free water was injected into the aquifer. The results demonstrated that the model calibrated to electrical observations coupled with U(VI) surface complexation model developed in the laboratory had significant predictive capability of field transport. A combined analysis of data from the laboratory experiments and field tracer tests is being used to evaluate upscaling approaches at the plume scale. Ultimately, plume-scale predictions of U(VI) transport for 16 years (1998-2013) will be compared with measured values in the aquifer, with upscaling of reactive transport parameters in accordance with the meter-scale studies.

NAME: Gary Curtis
ORGANIZATION: U.S. Geological Survey
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Multiscale Assessment of Prediction Uncertainty in Coupled Reactive Transport Models

ABSTRACT: Reactive transport simulations provide a systematic framework for integrating hydrologic and biogeochemical conceptual process models into a quantitative description of subsurface behaviors, which can then be used to project future concentrations. Assessing the uncertainty of these projections is difficult, because subsurface environments are open and complex, and subject to multiple interpretations and conceptualizations. This challenge is addressed using the method of multimodel analysis, in which model predictions are based on a weighted average of predictions of multiple plausible models, each of which is associated with a model averaging weight estimated from a maximum likelihood Bayesian model averaging approach.

The model averaging approach was evaluated for uranium transport at the Naturita UMTRA site using available data at the batch, column and tracer-test scale and in synthetic 3D simulations at the plume scale. At the batch and column scales, significant uncertainty results from imperfect knowledge of the adsorption reactions that immobilize uranium at the mineral surfaces as well as auxiliary reactions such as speciation and ion exchange. At the tracer test scale and especially in the 3D plume scale, additional uncertainty results from imperfect knowledge of the distribution of the reactive facies that describe the flow, transport and reactions. Model averaging had superior predictive coverage in both the column and tracer test analyses. The results for the synthetic physically and geochemically heterogeneous 3D study showed little support for oversimplified models such as those with homogeneous layers or zonal distributions of reactive facies. Heterogeneous distributions of reactive hydrofacies generally performed well; in some but not all instances these models gave superior predictions relative to model averaging. Model averaging had superior predictive coverage by considering model uncertainty. Parametric and conceptual model uncertainty for the stimulated bioreduction of U(VI) by microbial processes at the Rifle IFRC site was evaluated using a set of synthetic observations generated by a 3D reactive transport simulation of the Big Rusty field experiment. The ability to parameterize a comprehensive reaction network using a 1D model of the simulated 3D system was evaluated using sensitivity analysis and parameter estimation methods. Evaluation of the 1D approach was based on the ability of the calibration to estimate the known parameter values used in the 3D simulation, and on the suitability of the resulting parameter uncertainty estimates used in assessing predictive uncertainty. Results indicated that, although the 1D model can provide concentrations of key constituents that are representative of the 3D system, spatial variability in groundwater flow that is unresolved in the 1D abstraction can significantly bias the estimated reaction parameters. Derived linear parameter uncertainty estimates tended to be much smaller than indicated by the known conceptual errors. Without considering the impact of these conceptual errors, predictive uncertainty could be significantly underestimated.

NAME: Frederick Day-Lewis
ORGANIZATION: US Geological Survey
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Geoelectrical Measurement of Multi-scale Mass Transfer Parameters

ABSTRACT: Evidence of dual-domain mass transfer (DDMT) includes long "tailing" behavior and concentration rebound during aquifer remediation. The lack of experimental methods to verify and measure mass transfer in-situ independently of tracer breakthrough results in significant uncertainties in estimates of controlling parameters. Our objectives are to develop geophysical strategies to measure mass-transfer parameters over a range of spatial scales, and to demonstrate these strategies to produce estimates of mass-transfer parameters for Hanford 300 Area materials. Here, we assess the utility of time-lapse electrical resistivity (ER) and complex resistivity (CR) to improve the basic and site-specific understanding of mass transfer. During our final year of funding, we focused on (1) ER and CR laboratory experiments; (2) comparison of ER and CR results to nuclear magnetic resonance (NMR) measurements of mobile and immobile porosity; and (3) pore-network modeling of the electrical signature of mass transfer. Column ER/tracer-test experiments were performed using two samples of the porous zeolite clinoptilolite, which is a known dual porosity medium. We used glass beads and well sorted sand as two reference samples in which tailing behavior is not evident. Parametric sweeps using the model STAMMT-L identified best-fit DDMT parameters for the range of samples studied.

A comparison of solute transport behavior for the two zeolites revealed contrasting DDMT characteristics. For example, longer solute residence times were evident for the finer grained zeolite, for which NMR spectra indicate greater immobile porosity. The utility of CR methods for determining DDMT characteristics is ongoing. Debye decomposition analysis of CR spectra revealed a dominant relaxation time that appears to be controlled by grain size, which may have limited value for assessing mass-transfer properties. There is, however, an observed increase in polarization associated with short relaxation times with increasing immobile porosity as measured by NMR. From this we infer that the CR spectra are sensitive, in these examples, to the intra-grain porosity and hence physical characteristics that influence mass transfer.

Pore-network models qualitatively reproduce the hysteresis observed in time-lapse ER but indicate that the bicontinuum Archie model used previously systematically over predicts the contribution of immobile porosity to bulk conductivity. Alternative petrophysical models have been developed to account for different internal connectivity for mobile and immobile domains, providing a superior fit to the pore-network simulations of the bulk-fluid conductivity relation.

Infiltration and tracer experiments were conducted to assess the DDMT properties of the vadose zone in the Hanford Integrated Field Research Challenge well field in July of 2012. Data exhibit DDMT behavior. Analysis involves calibration of models to the breakthrough data and comparison to the electrical measurements. Publications on results from zeolites and pore-network modeling are in preparation. To date, three papers from this project have been published, and a fourth is undergoing revision. Ongoing work focuses on (1) analysis of field-experimental data, (2) development of the CR-NMR spectra analysis combining additional measured physical properties (e.g. surface area) (3) additional pore-scale modeling of the geoelectrical signature of DDMT.

NAME: Robert Ewing
ORGANIZATION: Iowa State University
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Effects of pore-scale physics on uranium geochemistry in Hanford sediments

ABSTRACT: The Hanford 300 Area sediments are mainly river cobble and gravel, with sands and fines (silt + clay) variably filling the voids in between. Fines comprise only 1.78% of the total sediment mass, but hold a disproportionately large fraction of the total U. However, the coarser sediments (e.g., >2 mm), with their larger mass fraction, may serve as a long-term U release pool despite their lower U concentration. We hypothesized that slow U release at the 300 Area is partly due to low connectivity of intra-granular pores. The objectives of this project were (1) to evaluate the U distribution in 2-8 mm size sediments, (2) to determine whether low pore connectivity affects U distribution and release from Hanford 300 Area sediments, and (3) if so, to assess its implications for long-term release. Our approach integrates laboratory experiments and pore-scale network modeling. Laboratory experiments include stirred flow cell, column, and batch sorption approaches, with the resultant samples analyzed by ICP-MS instrumentation for multiple elemental concentrations in liquid samples. In addition, laser ablation (LA)-ICP-MS was conducted for elemental mapping of 2-8 mm sized basaltic clasts. Pore-scale network modeling was also abstracted into a finite difference model that accounts for low pore connectivity effects on porosity and diffusion.

This past year (operating under a no-cost extension) we:

1) Collaborated with scientists of PNNL and Florida State University (FSU) on uncertainty analysis of an elution experiment (reported last year) measuring uranium desorption from different size fractions (<75 µm, 75-500 µm, 500-2000 µm, 2-8 mm, and a <2 mm composite). Using the experimental data collected from this project, a PhD student at FSU presented analysis at the 2013 AGU Fall Meeting, and is preparing a manuscript for publication to *Water Resources Research*.
2) Extended our own analysis of the elution data to consider the effect of having a range of particle sizes, rather than a single size. This analysis generalizes our earlier work published in *Water Resources Research*.
3) Extended our finite-difference model of diffusion from porous media with low pore connectivity, to account for non-linear sorption isotherms.

NAME: Scott Fendorf
ORGANIZATION: Stanford University
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Subsurface Conditions Controlling Uranium Retention Pathways

ABSTRACT: Stimulation of microbial uranium reduction in the subsurface can lead to substantial quantities of this toxic element being immobilized, but the potential for re-oxidative mobilization causes long-term stabilization to be technically challenging. Within natural environments, however, 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 the molecular mechanisms by which uranium is retrained by iron oxides and conditions optimal for its retention.

In order to examine the mechanism of uranium incorporation within iron oxides, and conditions conducive to its incorporation, we conducted a series of batch experiments coupled with spectroscopic and microscopic analysis of the reaction products. Through our experiments, we determine: *(i)* the oxidation state of incorporated U, *(ii)* the effects of calcium and carbonate (influencing U aqueous speciation) concentration, *(iii)* the pathway-dependence on Fe(II) and U(VI) concentrations, and, *(iv)* the competitiveness of U incorporation versus U reductive precipitation (to UO_2). A series of batch reactions with ferrihydrite were conducted at pH ~7, [U(VI)] from 1 to 170 µM, [Fe(II)] from 0 to 3 mM, [Ca] at 0 or 4 mM. 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 was incorporated into goethite. Uranium incorporation was a particularly dominant retention pathway at U concentrations ≤50 µM independent of U(VI) speciation, accounting for 70-80% of total U. With increasing U(VI) and Fe(II) concentrations, U(VI) reduction to UO_2 became more prevalent, but U incorporation remained an operative retention pathway. However, at high Fe(II) concentrations (3 mM), reduction to U(IV) and precipitation of UO_2 dominated. We further investigated the impact of mineralogical impurities common to the subsurface and found that although Al can inhibit ferrihydrite transformation, U(VI/V) incorporation occurred even at Al contents as high as 20% in Al-ferrihydrite. The combination of Ca-UO_2-CO_3 aqueous complexes and structural Al in ferrihydrite, however, resulted in limited incorporation or reduction. Our results demonstrate that U incorporation can be a major U retention pathway across a variety of aqueous phase and mineralogical conditions. 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.

NAME: Franz Geiger
ORGANIZATION: Northwestern University
PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Interaction of Cr(III) and Cr(VI) with ALD-Hematite Studied by Second Harmonic Generation

ABSTRACT: Iron oxides are a ubiquitous class of compounds that are involved in many biological, geological, and technological processes, and the Fe(III)/Fe(II) redox couple is a fundamental transformation pathway; however, the study of iron oxide surfaces in aqueous solution by powerful spectroscopic techniques has been limited due to “strong absorber problem”. In this work, atomic layer deposition (ALD) thin films of polycrystalline α-Fe_2O_3 were analyzed using the Eisenthal chi$^{(3)}$ technique, a variant of second harmonic generation (SHG) that reports on interfacial potentials. By determining the surface charge densities at multiple pH values, the point of zero charge was found to be 5.5 ± 0.3. The interaction of aqueous Fe(II) at pH 4 and in 1 mM NaCl with ALD-prepared hematite was found to be fully reversible and to lead to about 4 times more ferrous iron ions adsorbed per square centimeter than on fused-silica surfaces under the same conditions. The data are consistent with a recently proposed conceptual model for net Fe(II) uptake or release that is underlain by a dynamic equilibrium between Fe(II) adsorbed onto hematite, electron transfer into favorable surface sites with attendant Fe(III) deposition, and electron conduction to favorable remote sites that release and replenish aqueous Fe(II). Then, the chi$^{(3)}$ technique was used to investigate the adsorption of Cr(III) and Cr(VI) to the hematite/water interface under flow conditions at pH 4 with 10 mM NaCl. We observed partially irreversible adsorption of Cr(III), the extent of which was found to be dependent on the concentration of Cr(III) ions in solution. This result was confirmed using X-ray photoelectron spectroscopy. The interaction of Cr(III) with hematite is compared with the adsorption of Cr(III) to the silica/water interface, which is the substrate for the ALD-prepared hematite films, and found to be fully reversible under the same experimental conditions. The observed binding constant for Cr(III) interacting with the silica surface was found to be $4.0(6) \times 10^{3}\ M^{-1}$, which corresponds to an adsorption free energy of −30.5(4) kJ/mol when referenced to 55.5 M water. The surface charge density at maximum metal ion surface coverage was found to be 0.005(1) C/m^{2}, which corresponds to 1.0×10^{12} ions/cm^{2} assuming a +3 charge for chromium. In contrast, the observed binding constant for Cr(III) interacting reversibly with the hematite surface was calculated to be $2(2) \times 10^{4}\ M^{-1}$, corresponding to an adsorption free energy of −35(2) kJ/mol when referenced to 55.5 M water. The surface charge density at maximum metal ion surface coverage was found to be 0.004(5) C/m^{2} for the reversibly bound chromium species, which corresponds to 8.3×10^{11} reversibly bound ions per cm^{2}, again assuming a +3 charge of chromium. The data also allows us to estimate that about 6.7×10^{12} Cr(III) ions are irreversibly bound per cm^{2} hematite at saturation coverage. The results of this investigation suggest that the use of hematite in permeable reactive barriers, for cost-effective chromium remediation, allows for Cr(III) remediation at very low concentrations through adsorptive and redox processes but quickly renders the barriers ineffective at high chromium concentrations due to surface saturation.

NAME: Yuri Gorby
ORGANIZATION: Rensselaer Polytechnic Instituteq
PROGRAM AFFILIATION: SBR

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

ABSTRACT: Research conducted at the University of Southern California, Montana State University, and now at Rensselaer Polytechnic Institute in Troy, New York, embraces controlled cultivation approaches for controlling and optimizing the production and activity of extracellular conductive protein filaments called 'bacterial nanowires' by diverse groups of microorganisms.
The objective of our collaborative project is to evaluate the contribution of conductive bacterial nanowires on the fate and transport of uranium and chromium in contaminated subsurface systems.

During the past 2 years, we have developed and applied controlled-cultivation techniques for optimizing the production of conductive bacterial nanowires by 2 organisms isolated from contaminated sediments within the DOE National Lab complex. *Geobacter daltonii* FRC32^{T}is an iron(III) and uranium(VI)-reducing bacterium isolated from uranium-contaminated subsurface sediments at the DOE ORFRC. *Desulfovibrio vulgaris* RCH-1 is a sulfate-reducing bacterium that was isolated from chromium-contaminated groundwater at the 100H Hanford Site. Both organisms produced branched extracellular appendages in response to electron acceptor limited conditions, with ferric nitrilotriacetic acid (Fe(III)-NTA) provided as electron acceptor for *G. daltonii* FRC32^T and sulfate provided for *D. vulgaris* RCH-1 in chemostat and biofilm reactors, respectively. Amending the medium with amino acids to support the production of protein increased the production of extracellular filaments under electron acceptor limitation. Branched appendages from *G. daltonii* FRC32^{T}were confirmed to be electrically conductive nanowires using conductive atomic force microscopy. Attempts to evaluate the conductive properties of *D. vulgaris* RCH-1 are ongoing.

The influence of *G. daltonii* FRC32^T and *D. vulgaris* RCH-1 on fate and transport of uranium and chromium will be evaluated using 2D-flow columns designed and manufactured at RPI. Conditions within these flow columns will be manipulated to control the production of bacterial nanowires and other components of the extracellular polymeric matrix. Information gained from this research will be used to better understand the biogeochemical processes that influence contaminant transport at Hanford and the Oak Ridge Integrated Field Research Center. Understanding the components and mechanisms of charge transfer to extracellular electron acceptors by this and other environmentally-relevant organisms is an important step in realizing their full potential as tools for remediation of contaminated subsurface systems.

NAME: Kim Hayes
ORGANIZATION: University of Michigan
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Assessing the Role of Iron Sulfides in the Long-Term Sequestration of Uranium by Sulfate Reducing Bacteria (SRB)

ABSTRACT: This UM/ASU research seeks to identify how iron-sulfide minerals can inhibit the oxidation rate of reduced U solids formed by sulfate reducing bacteria (SRB). SRB normally utilize sulfate as a terminal electron acceptor and produce sulfide that precipitates with Fe(II) to form iron-sulfide (FeS) solids. At DOE sites contaminated with U, SRB can also reduce aqueous-phase U(VI) to insoluble U(IV) solids such as uraninite ((UO_2(s)). SRB can accomplish U(VI) reduction either directly by enzymatic electron transfer processes or indirectly through chemical reduction by the sulfides species produced. ***The hypothesis of this study is that iron sulfides inhibit the kinetics of re-oxidation of U(IV) to U(VI) when oxidants such as oxygen, nitrite, or Fe(III) are introduced.***

In the past year of this project, we achieved significant progress on all three major tasks: (1) evaluating the impact of a range of iron sources in biogenic FeS production under reducing conditions by *Desulfovibrio vulgaris*, (2) flow-through reactor studies of the inhibition of the oxidation rates of reduced U(IV) solids by FeS, and (3) packed sediment column studies for assessing the abiotic oxidation dynamics of U(IV) solids in the presence and absence of biogenic FeS under the influence of dissolved oxygen (DO) and nitrite.

Various iron sources were evaluated for biogenic FeS production by *D. vulgaris* in batch experiments with pyruvate as the electron donor, including soluble Fe(II) and Fe(III) and solid Fe(III) (hydr)oxides. When pyruvate was the electron donor, *D. vulgaris* produced distinct sulfate- and Fe(III)-reduction patterns and biogenic FeS characteristics. When soluble Fe(II) or Fe(III) was the iron source, simultaneous reduction of sulfate and soluble Fe(III) occurred along with the rapid utilization of pyruvate. Furthermore, the greater proton production during pyruvate fermentation (compared to lactate) lowered the pH, which led to more crystalline FeS formation. With solid-phase Fe(III) as the electron acceptor, complete and more rapid pyruvate consumption (compared to lactate) led to more FeS production and vivianite precipitation due to the greater accumulation of soluble Fe(II).

Continuously stirred tank reactors (CSTRs) were used for examining the inhibition mechanism and kinetics of UO_2 oxidation by mackinawite under oxic groundwater conditions. Experiments were conducted as a function of pH, calcium, FeS content, and DO concentrations to assess the impact of geochemical conditions on UO_2 oxidation kinetics. Results consistently show that FeS serves as an effective oxygen scavenger to inhibit the oxidation of UO_2. The solution pH influences UO_2 oxidative dissolution by shifting FeS oxidation mechanism. The presence of Ca^{2+} in the groundwater leads to the formation of passivation layer on UO_2 surfaces, which moderately reduces UO_2 dissolution rate. The UO_2 dissolution rate is strongly dependent on the concentration of DO and FeS solids in groundwater, with lower rate at lower DO levels and higher FeS content.

Packed column flow-through experiments were used to assess the abiotic oxidation dynamics of uraninite by nitrite and DO in natural sediments in the presence and absence of biogenic FeS. After acetate-induced bioreduction of Rifle sediments in parallel columns, one with sulfate present and one

without, gamma radiation was used to sterilize sediments before the oxidation reaction was initiated. The study shows that abiotic UO_2 oxidation by nitrite is essentially insignificant in comparison to oxidation by DO. Additionally, sediments containing FeS minerals significantly inhibit UO_2 oxidation compared to sediment without FeS present. In both columns, significant amounts of sediment-bound U remained after extensive oxidation, suggesting a U adsorption or other solid-phase incorporation mechanism related to the biologically reduced sediments.

NAME: Heileen Hsu-Kim
ORGANIZATION: Duke University
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Dissolution Potential and Bioavailability of Nanoscale Mercury Sulfides

ABSTRACT: 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. In benthic sediments and other anaerobic settings, inorganic mercury Hg(II) is typically coordinated to reduced sulfur-containing ligands including inorganic sulfide and natural organic matter. This presentation will discuss research to characterize and identify the forms of Hg(II) that are bioavailable to methylating bacteria. We performed laboratory experiments to demonstrate that the combination of Hg(II), sulfide, and dissolved organic matter (DOM) in solution results in a heterogeneous mixture of dissolved Hg(II) complexes, amorphous Hg-S-DOM nanoparticles, and crystalline HgS particles. The composition of this mixture evolves over time and is not necessarily predicted by equilibrium speciation models. Moreover, in bacterial cultures of sulfate reducers, the production of methylmercury depended on the form of mercury added. Net production of MeHg was greatest in cultures receiving dissolved Hg, while cultures receiving Hg-S-DOM nanoparticles generated 20-40% less MeHg in most cases, depending on the productivity of methylating microbes. This result was in stark contrast to the minimal production of methylmercury in all cultures amended with microcrystalline metacinnabar HgS. The production of MeHg in the nanoparticle exposures also depended on the age of the nanoparticle stock solutions. Small angle X-ray scattering and X-ray absorption spectroscopy was used to characterize the structure of the nanoparticles as they changed in their stock solution. The results indicated that organic matter was altering the rate of crystal ripening and agglomeration of the nanoparticles. These changes resulted in nanoparticles with a lower dissolution potential when added to bacterial culture media in the methylation experiments. These experimental results point to the need of a kinetics-based reaction model that links inorganic mercury speciation (including nanoscale species) and methylation potential. Overall we anticipate that this approach may enable the consideration of nanoscale geochemistry for predictions of Hg reactivity and bioavailability in the environment.

NAME: Peter R. Jaffe
ORGANIZATION: Princeton University
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Evolution of Methanogenesis during Biostimulation of Alluvial Sediments

ABSTRACT: We have been conducting a long-term column experiments to study the link between biostimulation and changes in permeability. Nine columns (4.8 cm ID, 30 cm long) were built with side ports at 2 cm intervals, which allow for dissolved species sampling and pressure change measurements along their vertical axis. The experiment has been operating now for approximately 700 days. One column is equipped with electrodes to determine the induced polarization (IP) and link this to changes in permeability and to IP measurements that have been conducted at Rifle during previous biostimulation experiments. Columns were filled with Rifle background sediment and the water being pumped into the columns is Rifle groundwater that is being shipped to the laboratory at monthly intervals. The experiment is divided into an acetate biostimulation phase of 488 days and in a post biostimulation phase that has now been operating for 212 days. Columns have been sacrificed at regular intervals during the biostimulation and the post-biostimulation period to analyze for solid-species changes and total microbiological quantification. Results to date have shown that there was a small and gradual (seemingly linear) increase in pressure over time during the first 200 days of biostimulation. Then, after about 220 days of biostimulation, we see a significant change in pressure along the longitudinal axis of the columns. This pressure increase occurred approximately 50 days after sulfate was completely reduced. Effluent analyses show that by this time, methane was near solubility. Microbiological analyses have shown that for the first 200 days of the biostimulation total bacterial numbers were similar to methanogen numbers (~ 10^8 cells/g). For columns sacrificed after 200 days of biostimulation, methanogen numbers were an order of magnitude higher than total bacteria. They have remained higher also troughut the post-biostimulation period. Although Rifle field experiments, focusing on dissolved groundwater samples have not reported significant presence of *Archaea*, these results, that focused on sediment analyses, seem to indicate that *Archaea*, in this case methanogens, might be a key organism competing for electron donors during biostimulation.

During the post biostimulation period, methane concentration in the effluent decreased within 20 days by 3 orders of magnitude, from solubility to about 10^{-6} M, and remained at that concentration without much change until this date.

In terms of permeability changes in response to biostimulation, we conclude that biogas formation has a higher impact than the precipitation of mineral phases and/or biomass buildup, and that these changes are reversible. Towards the end of the biostimulation period, the average permeability in the columns had decrease by one order of magnitude.

A conservative estimate of the acetate converted to methane over the 700-day duration of the experiment is 12% on a molar base. This is a lower-limit estimate, based on cumulative acetate consumed during the biostimulation period (488 days), and methane monitored in the effluent up to 700 days. It does not include any methane oxidation during the post stimulation phase, and there was a short period (~ 35 days) where methane gas in the effluent was not quantified.

NAME: Peter R. Jaffe
ORGANIZATION: Princeton University
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Uranium Transport across Ground Water Surface Water Interfaces: Effect of Wetland Plants on the Sediment Biogeochemistry

ABSTRACT: Discharges of uranium containing groundwaters to surface waters are a concern at several wetlands, including some at DOE facilities. Sharp biogeochemical transitions that occur near wetland plants may greatly affect the fate of many redox-sensitive metals and radionuclides, including uranium. Our research investigates how wetland plant roots affect sediment biogeochemistry and uranium mobility with respect to both short- and long- term goals.

We have formulated three primary hypotheses: (1) oxygen released by wetland plant roots oxidizes iron to Fe(III), providing favorable conditions for iron reducers that also reduce U(VI) to much less mobile U(IV), (2) microorganisms, including iron/uranium reducing microorganisms, are stimulated by organic carbon provided by wetland plants via root exudates and root turnover, and (3) U(IV) remains stable for extended time periods in wetlands that are often anaerobic and nitrate poor. Testing these hypotheses requires examining key iron and uranium reducing microorganisms, along with the spatial distribution and speciation of uranium and other important chemical species.

We have developed small-scale (700 mL) up-flow vegetated (*Typha latifolia* or *Scirpus acutus*) and non-vegetated mesocosms, and are operating them in our greenhouse in an up flow mode to simulate groundwater to surface water discharge and to test above hypotheses. The porous medium used was sand augmented with (0.2 wt-%) sediment collected from Savannah River Site (SRS) wetlands, in order to provide an appropriate microbiological seed. Siderite was supplied at the bottom of some of the microcosms for each plant treatment, in order to buffer the pH and provide an iron source since the sand had a very low iron content. To differentiate biogeochemical changes in sediments near roots and sediments that are not in direct contact with roots, several small bags (70 micron-mesh nylon) were filled with 1 to 3 grams of the sand/sediment mixture and placed at different locations in the mesocosms allowing for the retrieval of sediments from a root-exclusion zone. A modified Hoagland solution was pumped through the mesocosms at a rate of 100 to 150 mL per day. After the mesocosm plantings had been established, uranium was supplied into the influent via peristaltic pumps, resulting in an estimated 20 uM influent uranium concentration. Mesocosms were then operated for 80 days, and dissolved species were periodically sampled. The mesocosms were subsequently sacrificed and analyzed for solid-associated chemical species as well as microbiological characterization.

Results indicate differences between the mesocosms planted with *Typha latifolia* (common cattail), *Scirpus acutus* (hardstem bulrush), and no plant controls, as well as between mesocosms with and without the siderite iron source. Planted mesocosms showed increasing Fe concentrations in solution with elevation. *Typha latifolia* roots show larger proportions of Fe in the oxidized state than *Scirpus acutus* roots. Total bacterial populations as well as Geobacter sp. numbers were highest on roots (on a per gram basis), followed by sediments near roots, and lowest in the root-exclusion zones.

NAME: Kristina Keating
ORGANIZATION: Rutgers University
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Integrated geophysical measurements for bioremediation monitoring: combining NMR, magnetic methods and SIP

ABSTRACT: Our research aims to develop borehole measurement techniques to monitor subsurface processes, such as changes in pore geometry and iron/sulfur geochemistry, associated with remediation of heavy metals and radionuclides. Previous work has begun to identify methods that are capable of surveying the subsurface environment. One such method, spectral induced polarization (SIP), has been used to monitor the progress of subsurface contaminant remediation; however, its interpretation is of limited value in isolation. In our research we aim to combine measurements from multiple geophysical methods, i.e. nuclear magnetic resonance (NMR), and magnetic susceptibility (MS), with SIP, to allow us to reduce or overcome the limitations associated with using one measurement alone. The integration of measurements from multiple geophysical methods, each sensitive to mineral form and/or mineral-fluid interfaces, will provide better constraints on subsurface biogeochemical processes and evolution of pore geometries and significantly improve our understanding of processes impacting contaminant remediation.

In the first year of the research project, NMR and MS borehole logging measurements were collected at the Rifle Integrated Field Research Challenge (IFRC) site. The Rifle IFRC site is located at a former uranium ore-processing facility in Rifle, Colorado. Although removed from the site by 1996, leachate from spent mill tailings has resulted in residual uranium contamination of both groundwater and sediments within the local aquifer. Ongoing studies at the site include an acetate amendment strategy, in which stimulation of native microbial populations by introduction of a carbon source serves to alter local redox conditions and immobilization of uranium in insoluble forms. NMR and MS logging measurements were taken before, during, and after acetate amendment. Changes in these signals were expected to correlate with changes in redox conditions and iron speciation. Experimental data were collected from two wells upstream of the acetate amendment, used as controls, and from three downstream wells.

The MS measurements revealed vertically stratified magnetic mineralization, likely the result of a detrital magnetic fraction within the bulk alluvium. Data were highly replicable over the monitoring interval, with little to no change observed in the MS measurements, suggesting negligible production of magnetic phases (e.g. magnetite, pyrrhotite) as a result of sulfidogenesis. NMR measurements had high levels of noise contamination requiring significant signal processing, and analysis suggests that any changes due to stimulated microbial activity may be difficult to differentiate from simultaneous changes in water content.

The second year has focused on collecting laboratory NMR, MS, and SIP measurements on columns packed with sediments from the Rifle IFRC site as the columns are amended with acetate. The column experiments are designed to simulate field conditions. As of this date, columns that are capable of being used for SIP, MS and NMR measurements have been designed and built and the experiments are being initialized. In addition to the geophysical measurements, changes in the geochemistry and pore geometry inferred from these ongoing measurements will be verified by standard, independent

NAME: Li Li
ORGANIZATION: The Pennsylvania State University
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Effects of illite spatial distribution on Cr(VI) sorption dynamics

ABSTRACT: The spatial distribution of clay can have a large impact on the sorption of contaminants, therefore affecting their transport and fate in the natural subsurface. In this work, the effects of illite spatial distribution on Cr(VI) adsorption was examined using column experiments and reactive transport modeling under several flow rate conditions. Three columns were set up with the same volume fraction of illite (10%): the Mixed column has illite evenly mixed within a quartz matrix; the Flow-transverse column has illite distributed in one horizontal zone in the direction that is vertical to the main flow; the Flow-parallel column has illite distributed in one cylindrical zone in the direction parallel to the main flow direction. Cr(VI) adsorption and desorption column experiments were carried out under flow velocities of 0.6, 2.9, and 14.8 m/day. Two-dimensional reactive transport modeling was used to understand the role of illite distribution in determining Cr(VI) sorption kinetics.

The difference in the sorption kinetics in the three columns varies, depending on the flow conditions. Under the slower flow rate of 0.2 ml/min, the Cr(VI) adsorption behavior was very similar for the Mixed and Flow-transverse columns. Sorption of Cr(VI) occurred immediately following the injection of an inlet solution with a pH of 4.0. The sorption occurred fast early on and reached 80% of Cr(VI) sorption capacity of the columns at about 12 residence times. Sorption slowed down after that and reached full capacity with another 30 – 40 residence times. In contrast, sorption in the Flow-parallel column occurred at a much lower rate early on, reaching about 80% sorption capacity within about 30 residence time, about 2.5 times slower than the other two columns. The 2D reactive transport model shows that the Cr(VI) sorption in this column is limited by the rate of mass transport at the illite-quartz interface. Cr(VI) was only adsorbed on the illite-quartz interface early on and gradually percolated into the illite zone over time. The transverse dispersivity, a measure of the mass transport rate, plays a key role in determining the sorption kinetics of the Flow-parallel column. At the flow velocity of 2.9 m/day, the difference among the three columns is similar to the difference at the flow rate of 0.6 m/day. At the flow rate of 14.8 m/day, the three columns show almost exactly the same sorption behavior with overlapping breakthrough curves. With increasing flow rates, the overall sorption capacity of all three columns also decreases.

NAME: Frank Loeffler

ORGANIZATION: University of Tennessee & Oak Ridge National Laboratory

PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Exploring the Responses of Metal-Reducing Bacteria to Fluctuating Redox Conditions

ABSTRACT: Diverse groups of microorganisms and abiotic reactions affect the oxidation state of redox-active metals, and oxic-anoxic transition zones are hotspots for metal cycling. Redox transition zone processes are relevant controls for the fate of radionuclides such as uranium, which is mobile as U(VI) but only sparingly soluble in its U(IV) form. Metal-reducing bacteria adapted to life in oxic-anoxic transition zones play important roles for controlling U mobility. To explore the effects of changing redox conditions on the microbiology contributing to ferric iron and U(VI) reduction, an x-ray accessible plexiglass column with sampling and outflow ports along the length of the column has been constructed. Initial tests of the column packed with acid washed sand and FeOOH-coated sand showed that changes in the distribution and speciation of Fe resulting from the flow of dissolved sulfide can be monitored with synchrotron x-ray spectroscopy using the intact column. Another column design allows the infusion of different (e.g., oxic and anoxic) feed solutions from both ends leading to the formation of a controllable redox gradient and is being used to investigate the responses of microbes to fluctuating oxic-anoxic transition zones.

A number of microbes have been implicated in metal reduction and tools to directly measure their metal-reducing activity are desirable. We applied high precision mass spectrometry and demonstrated that a significant U isotopic fractionation occurs during microbial U(VI) reduction, with U(VI) becoming isotopically lighter with progressive amounts of reduction. Enrichment factors (ε) measured with different metal-reducing isolates (i.e. *Geobacter, Anaeromyxobacter, Shewanella* and *Desulfitobacterium*) tend to range between 0.7‰ and 1.0‰, and follow the expected inverse relationship between reaction rate and the magnitude of fractionation. Only *Shewanella* sp. strain NR exhibited unusual near-zero fractionation at low U concentrations, suggesting that multiple U reduction pathways with different mechanisms (and thus different isotopic fractionation) contribute to U(VI) reduction. Further, metaproteomics analysis identified specific *c*-type cytochromes expressed in cultures of *Anaeromyxobacter dehalogenans* strain 2CP-C grown with manganese oxide as electron acceptor suggesting that the presence and abundance of the specific transcripts and/or proteins provides information about the physiological status of the organism. The analysis of samples obtained from defined laboratory studies and groundwater samples collected at field sites demonstrates the value of the new tools to assess, monitor, and predict reductive processes affecting the redox speciation (i.e., mobility) of relevant metals and radionuclides.

NAME: Derek Lovley
ORGANIZATION: University of Massachusetts
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: The Mechanism for Fe(III) Oxide Reduction in Geobacter sulfurreducens

ABSTRACT: The mechanisms for Fe(III) oxide reduction in *Geobacter* species are of interest because of its important role in global carbon cycling. This is also of specific interest to the Subsurface Biogeochemical Research Program because *Geobacter* species, growing primarily via Fe(III) oxide reduction, have been shown to be important agents in the bioremediation of uranium-contaminated groundwater. There has been substantial debate about the mechanisms for Fe(III) oxide reduction in *Geobacter* species. One model is that electrons are transported outside the cell along proteinaceous pili that have metallic-like conductivity and that the multi-heme *c*-type cytochrome OmcS, which is specifically localized along the pili, facilitates electron transfer from the pili to the Fe(III) oxide. The alternative model is that outer-surface *c*-type cytochromes not associated with pili are the primary electrical contacts with Fe(III) oxides. Conclusively differentiating between these two hypotheses has been difficult, in part because of the non-specific reduction of Fe(III) by many different cytochromes *in vitro*. Furthermore, genetic approaches have often yielded strains in which the deletion of a single gene influenced the production and/or localization of multiple proteins.

In order to investigate Fe(III) reduction mechanisms further, a strain of *G. sulfurreducens*, designated Aro-5, was constructed which produced pili with diminished conductivity. This was accomplished by modifying the amino acid sequence of PilA, the structural pilin protein. An alanine was substituted for each of the five aromatic amino acids in the carboxyl terminus of PilA, the region in which *G. sulfurreducens* PilA differs most significantly from the PilA of microorganisms incapable of long-range extracellular electron transport. Strain Aro-5 produced pili that were properly decorated with OmcS. Other abundant outer-surface *c*-type cytochromes, such as OmcZ, were properly expressed and localized. However, the Aro-5 pili had greatly diminished conductivity and Aro-5 cultures were severely limited in their capacity to reduce Fe(III) compared to the control strain. The capacity of the Aro-5 strain to produce electrical current with a graphite anode serving as the electron acceptor was less than 10 % of the control strain and the conductivity of the Aro-5 biofilms was 10-fold lower than the control strain. These results further demonstrated that loss of pili conductivity reduced the capacity for long-range electron transport. Thus, the expression of outer-surface c-type cytochromes is insufficient for Fe(III) reduction in *G. sulfurreducens*. The pili of *G. sulfurreducens* must be conductive in order for the cells to be effective in extracellular long-range electron transport.

Previous evidence for the alternative hypothesis, that *G. sulfurreducens* reduces Fe(III) with outer-surface *c*-type cytochromes not associated with pili, was the finding that deletion of gene GSU1501, which controls production of exopolysaccharide, inhibited Fe(III) oxide reduction. However, further examination of the GSU1501-deletion mutant revealed that this strain does not properly localize OmcS on the pili. OmcS is produced and is abundant in the extracellular matrix. Thus, the phenotype of the GSU1501-deletion mutant is also consistent with the model in which long-range electron transport is along the pili, which delivers electrons to OmcS for the final electron transfer to Fe(III) oxide.

These studies rule out the possibility that outer-surface *c*-type cytochromes can effectively facilitate Fe(III) oxide in the absence of pili conductivity and support the concept that long-range electron transport along pili is the primary mechanism for Fe(III) oxide reduction by *G. sulfurreducens.*

NAME: Derek Lovley
ORGANIZATION: University of Massachusetts
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Detailed Modeling of Uranium Mobility Under a Combined Influence of Microbial Activities and Geochemical Transformations

ABSTRACT: The mechanistic model of in situ uranium bioremediation requires a detailed representation of subsurface microbial metabolism and an accurate characterization of interactions between microbial and geochemical processes. The overall objective of this project is to develop a fine-scale computational framework capable of predicting uranium mobility under a combined influence of microbial activities and geochemical transformations.

We have made progress in both biotic and abiotic processes for achieving the project goal. 1) A preliminary pan-genome-scale metabolic model for subsurface *Geobacter* community was developed. The unique features of the metabolism suggest more of a necessity from studies of subsurface communities than from the subsurface isolates or from the non-subsurface model species. 2) The quality of the metabolic network reconstruction for subsurface *Geobacter* community was improved by removing thermodynamically infeasible loops with unrealistic high fluxes. 3) Physiological studies of the sulfate reducing bacteria, *Desulfobacter postgatei*, were conducted to evaluate the metabolic activity under electron donor-limiting and electron acceptor-limiting conditions, respectively. A genome-scale model of *Desulfobacter postgatei* was developed, providing some insights into the sulfate reduction pathways. 4) An optimized genome-scale metabolic model for *Anaeromyxobacter dehalogenan* (a unique bacteria with diverse metabolic capabilities such as uranium reduction) was developed, and a bi-level optimization algorithm for resolving energetic model inconsistencies (REMI) was implemented to remove the reactions with unrealistic high ATP production. 5) Computational thermodynamics based on the coupled oxidation-reduction reactions for geochemical transformation was integrated into a comprehensive reactive-transport model of in-situ bioremediation of U(VI), providing predictions and insights into the role of abiotic redox reactions that occur in systems with interplay between microbiological and geochemical processes. This approach helps to address some questions of interest, such as the reason why abiotic U(VI) reduction often takes place under laboratory conditions but has not been reported to play an important role under environmental conditions. The above-mentioned recent advances in modeling biotic and abiotic processes will help to ultimately build a fine-scale predictive model for computer-aided design of field-scale uranium bioremediation.

NAME: Derek Lovley
ORGANIZATION: University of Massachusetts
PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Remote, Real-Time Measurements of In Situ Rates of Microbial Activity in a Diversity of Soils and Sediments

ABSTRACT: Strategies to simply and inexpensively monitor the activity of microorganisms in soils and sediments are needed for studies on bioremediation and for assessing changes in microbial activity due to environmental perturbations, such as climate change. Current methods typically involve invasive sampling of the environment, which can alter microbial activities, and require the addition of tracers or indicators, adding complexity and expense. Furthermore, these traditional methods are not amenable to real-time monitoring of *in situ* activity.

We are developing a simple and inexpensive electrode-based method for monitoring rates of microbial activity in a wide diversity of anaerobic soils and sediments. Our strategy is based on the concept that the pathways for intermediary metabolism of organic carbon are similar in all anaerobic soils regardless of whether the terminal electron-accepting process is Fe(III) reduction, humics reduction, sulfate reduction, or methane production. In each type of soil, complex organic matter is fermented to simple intermediates, such as acetate and H_2, which are then consumed by the terminal respiratory processes. If a graphite electrode is inserted in anaerobic soil and connected to another electrode in contact with oxygen, then the electrode in the soil can serve as an alternative electron acceptor. Microorganisms colonizing the electrode surface will oxidize the acetate and other intermediates, produced from fermentation, with electron transfer to the electrode. The rate of this electron transfer is measureable as an electrical current. Thus, in the absence of any other complicating factors, it can be expected that the amount of current produced from an electrode in an anaerobic soil will be directly related to the rates of microbial metabolism in those soils or sediments.

This concept is being tested with a diversity soils and sediments in which different electron accepting processes predominate. Cores of freshwater methanogenic sediment were incubated at a range of temperatures to provide sediments with a range of rates of metabolism. Graphite electrodes were inserted at different depths in the sediments and electrically connected to graphite cathodes suspended in the overlying water through a resistor. Remarkably stable currents were recorded with higher currents at sediment depths or temperatures that were expected to have higher rates of microbial metabolism.

In order to directly compare current production with rates of microbial activity, the sediments near each electrode was sampled by subcoring and the subcores were injected with a [2-^{14}C]-acetate tracer. Production of $^{14}CH_4$ and $^{14}CO_2$ were monitored over time to determine the rates of acetate metabolism in the sediments. There was a strong positive correlation between the rates of microbial metabolism determined with the traditional [2-^{14}C]-acetate tracer techniques and the levels of current production. Similar studies were conducted on artic peat from the DOE Next-Generation Ecosystem Experiments (NGEE) Arctic project site in the Barrow Experimental Observatory near Barrow, Alaska. The correlation between rates of metabolism as determined with [2-^{14}C]-acetate and current production fell on the same line as for the methanogenic sediments, despite the fact that in some of the artic peat sediments Fe(III) reduction appeared to be the predominant terminal electron-accepting process. Electrode deployments at the NGEE site generally yielded *in situ* currents consistent with the laboratory studies.

NAME: Yi Lu
ORGANIZATION: University of Illinois at Urbana-Champaign
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Catalytic DNA Biosensors for Radionuclides and Metal Ions

ABSTRACT: We are developing novel field-portable catalytic DNA biosensors to detect and quantify bioavailable radionuclides such as uranium, technetium, strontium, and plutonium as well as metal contaminants such as mercury and chromium. The sensors will be highly sensitive and selective, not only for different metal ions, but also for different oxidation states of the same metal ion (such as U(IV) vs. U(VI), or Cr(III) vs. Cr(VI)). To achieve the goals, we are using the combinatorial biological technique called *in vitro* selection to obtain catalytic DNAs that are highly specific for a given radionuclide or metal ion. We also use state-of-the-art biochemical and biophysical techniques to elucidate the structural elements responsible for high selectivity. These DNA have been transformed into fluorescent or colorimetric sensors by labeling the DNA with fluorophores or gold nanoparticles through catalytic beacon and nanoparticle assembly technologies developed in the PI's group, with detection limit down to 11 ppt and over millions-of-fold selectivity of uranyl over other radionuclides and metal ions. These sensors have been developed into commercially available sensor products that allow detection and quantification of radionuclides and metal ions in less than 2 min.

In the past year, we have made significant progresses in three areas. First, we have developed label-free catalytic and molecular beacon containing an abasic site for sensitive fluorescent detection metal ions such as Pb^{2+}.[1] The label-free method can significantly simplify the sensing method and lower its costs. Second, having obtained highly sensitive and selective sensors for radionuclides and metal ions, we have elucidated structural features and mechanism for the high sensitivity and selectivity, such as the importance of peripheral sequences in determining the metal selectivity of a catalytic DNA.[2] This knowledge will be quite valuable for designing new sensors and chelating agents for radionuclides and metal ions. Finally, for the first time, we have now extended the catalytic DNA sensors in detecting uranyl in living cells using catalytic DNA gold nanoparticles probe that can readily enter cells and can serve as a metal ion sensor within a cellular environment.[3] Such a method can be generally applied to the detection of other radionuclides and metal ions using other catalytic DNA selected through in vitro selection.

Detecting and quantifying radionuclides and metal contaminants onsite and in real-time in a simple and cost-effective way will impact many other areas of research under the SBR program. For example, it will enhance geochemistry/biogeochemistry research by lowering the costs of characterization and by providing more accurate information of the radionuclides and metal contaminants at the DOE sites. This information will strengthen the correlations between results obtained from microbial ecology and community dynamic analyses and DOE site properties, improve the understanding of the mechanisms of biotransformation, and provide deeper insight into biomolecular science and engineering. Practical applications of these sensors will not only help assess the effectiveness of science-based solutions for remediation performed by researchers and engineers, but will also contribute to the long-term monitoring of DOE contaminated sites by DOE staff members, state and local regulation agents, and concerned citizens around the sites.

1. Panshu Song, Yu Xiang, Hang Xing, Zhaojuan Zhou, Aijun Tong and Yi Lu, Analytical Chemistry 84, 2916-2922 (2012)).
2. Kevin E. Nelson, Hannah E. Ihms, Debapriya Mazumdar, Peter J. Bruesehoff and Yi Lu, ChemBioChem 13, 381-391 (2012).
3. Peiwen Wu, Kevin Hwang, Tian Lan and Yi Lu, *J. Am. Chem. Soc.*, 135, 5254–5257 (2013).

NAME: Craig Lundstrom
ORGANIZATION: University of Illinois at Urbana-Champaign
PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Development of U isotope fractionation as an indicator of U(VI) reduction in U plumes

ABSTRACT: We are evaluating $^{238}U/^{235}U$ (as $\delta^{238}U$) as a tool for monitoring U(VI) reduction in the controlled field setting at the Rifle, CO IFRC site. Understanding the biogeochemical behavior of uranium in the subsurface will help to improve remedial strategies and long-term stewardship activities at DOE sites. We present $^{238}U/^{235}U$ (as $\delta^{238}U$) results for three Rifle IFRC field experiments: (1) the 2010–11 experiment, which combined bicarbonate-induced desorption of U(VI) and down-gradient acetate-induced bioreduction (21 and 25 days, respectively), (2) the subsequent 2011–12 experiment, which evaluated the impacts of prolonged bicarbonate and acetate amendments (94 and 72 days, respectively) and the impact of a second acetate injection and (3) the 2012–2013 reoxidation experiment.

Large variations in $\delta^{238}U$ accompany acetate-induced biostimulation under both iron reducing (2010–11) and sulfate reducing conditions (2011–12). In both cases, ^{238}U is preferentially reduced to U(IV), leaving the remaining groundwater U(VI) relatively enriched in ^{235}U ($\Delta^{238}U = -1.3$ and -1.9‰, respectively). Thus $\delta^{238}U$ in waters decreases as the U concentration drops from ~150–200 ppb U prior to the acetate injection to ~10 ppb after. For the 2010–11 experiment, groundwater U(VI) concentration and $\delta^{238}U$ quickly return in unison to background values within 113 days after the end of the acetate injection. During the post-injection phase, as concentrations rebounded, absence of $^{238}U/^{235}U$ greater than pre-injection values implies the primary source of U is advection of U(VI), rather than reoxidation of U(IV). This is particularly important as the long term success of this remediation technique depends on the stability of sequestered U(IV). Early results from the 2012–2013 reoxidation experiment suggest that as the dissolved oxygen injection proceeded, oxidation of U(IV) precipitates leads to both an increase in U concentration and $^{238}U/^{235}U$ of groundwater.

For 2010–11 samples impacted by both bicarbonate and acetate amendments, we observe an initial increase in U(VI) concentration (more than doubling) due to the bicarbonate desorption of U(VI) from mineral surfaces followed by a large drop in U(VI) concentration as acetate-induced reduction proceeds. As with the bicarbonate-only desorption experiment [1], U(VI) desorption resulted in no change in $^{238}U/^{235}U$; this ratio, however, changes with the onset of reduction with acetate amendment. $\delta^{238}U$ decreases quickly, then rebounds during the time of lowest dissolved U(VI) concentration, and finally increases slowly to background levels within 266 days from the end of the acetate injection. The much slower recovery is suggested to result from the slow exchange of newly advected U with the relatively light sorbed U (resulting from equilibration of sorption sites with light dissolved U(VI) during the biostimulation). Thus, bicarbonate-induced U desorption in combination with biostimulation increases the removal of U(VI) during biostimulation.

Our research demonstrates the potential for $^{238}U/^{235}U$ to detect U(VI) reduction in the subsurface and to distinguish between removal by reduction and relatively temporary processes such as sorption. Preliminary results from the latest experiment at Rifle suggest the $^{238}U/^{235}U$ technique can also be used to detect reoxidation of previously sequestered U.

[1] Shiel, A.E. et al. (2013) Environ. Sci. Technol. 47, 2535–2541.

NAME: Brian Mailloux
ORGANIZATION: Barnard College
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Linking As, Se, V, and Mn Behavior to Natural and Biostimulated Uranium Cycling

ABSTRACT: Biogeochemical redox cycles in groundwater systems frequently mobilize metals and metalloids that directly impact human health. These same biogeochemical cycles can also alter uranium speciation and mobility thus directly impacting groundwater quality at DOE legacy sites. Interestingly, the reducing conditions that immobilize uranium may be optimal for mobilizing metals such as As, Mn, Se, and V. These processes are occurring at the Department of Energy's Field Research Challenge (IFRC) site near Rifle, Colorado and offer a unique opportunity to study biogeochemical redox cycles. At well U01 near the Colorado river, natural redox fluctuations occur with changing river stages. When the river stage is high the aquifer appears oxidized. When the river stage is low the aquifer becomes reducing and Mn, As, and sometimes Fe becomes mobilized. Interestingly, little change in U concentrations are observed. During biostimulation at the IFRC As concentrations dramatically increase in the groundwater. During Fe(III) reduction, As levels increase to concentrations similar to levels observed in well U01 (~1.0 µM). However under sulfate reducing conditions As concentrations can be over ten times higher. Initial speciation work by IC-ICP-MS from samples collected during the "Best Western" experiment in 2011 indicated that arsenite was the dominant species during Fe(III) reduction but thioarsenates, in particular trithioarsenate, become dominant during sulfate reduction. No thioarsenites were observed. Across the flow field arsenic species also varied with a higher proportion of thioarsenic species located near the injection well. Speciation results were in close agreement with geochemical modeling. Future work will focus on examining the interplay between organic carbon sources and arsenic speciation during natural redox fluctuations observed during changes in river stage. In addition, we will also attempt to determine the source of organic carbon for the regions of the aquifer that are naturally reducing. The goal is to better understand redox cycling and the source of organic carbon in aquifer systems.

NAME: David Mays
ORGANIZATION: University of Colorado Denver
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Colloid Deposit Morphology and Permeability of Porous Media

ABSTRACT: Subsurface remediation and materials transport through soils depend on flow in porous media. Darcy's law states that such flow is proportional to permeability, which depends *in part* on porosity. However, when colloidal materials (such as clays, precipitates, or microbes) form deposits, the resulting permeability cannot be accurately predicted from porosity. This is a major challenge for subsurface remediation, casting doubt on models linking biological, geological, and chemical processes. It has been hypothesized that the morphology of colloid deposits—specifically, their fractal dimension—could be a critical aspect relating deposition and permeability. Until now, determining colloid deposit morphology within porous media at the relevant spatial scale is an unsolved problem. To address this issue, we have developed a unique extension of static light scattering to measure the fractal dimension of colloid deposits within refractive index matched (*i.e.*, transparent) porous media. The media in our flow column is Nafion, a synthetic material that becomes essentially transparent when saturated by a solution of isopropanol and water. We are studying the aggregation and deposition of colloidal polystyrene microspheres. Laser light scatters from the deposited colloids, but not from the transparent Nafion, such that the intensity of scattered light as a function of scattering angle indicates the fractal dimension.

While neither the solid nor fluid phase components are taken from natural environments, this system will permit us to study the relationship between deposit fractal dimension and flow within saturated columns under well characterized flow conditions. Currently, we are measuring how deposit fractal dimension varies with ionic strength, and how fluid velocity (*i.e.*, shear stress) dynamically changes deposit morphology.

In complementary research aimed at generalizing these laboratory results to field settings, we are also measuring the fractal dimension of suspended colloids in groundwater collected from the Old Rifle Integrated Field Research Challenge (IFRC) site in western Colorado. Other samples, to be analyzed in Summer 2013, will provide fractal dimension of mineral precipitates and microbial biofilms collected from laboratory models prepared in collaboration with Lawrence Berkeley National Laboratory.
The ultimate goal of this research is to create a clogging model linking environmental variables and colloidal phenomena to soil permeability, in order to reduce the associated uncertainty in models for subsurface remediation and materials transport.

NAME: Duane Moser
ORGANIZATION: Desert Research Institute
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Radiochemically-Supported Microbial Communities: A Potential Mechanism for Biocolloid Production of Importance to Actinide Transport

ABSTRACT: The US Department of Energy (DOE) conducted 828 underground nuclear tests at the Nevada National Security Site (NNSS) from 1951 to 1992. The resulting cavities, sterilized by conditions sufficient to melt rock, afford an opportunity to examine microbial ecology in a zone where the juxtaposition of radioactivity with varying rock types, temperature, chemistry and hydrology enables the study of processes controlling radionuclide transport. This project focuses on the hypothesis that radiogenic substrates such as H_2 at DOE sites may support the growth of microorganisms, and thus indirectly influence the mobility of redox-sensitive radionuclides. Consistent with this hypothesis were early project results (e.g. as reported at the 2012 SBR PI meeting) correlating the presence of both H_2 and SSU rRNA genes nearly identical to those of candidatus *Desulforudis audaxviator* in radioactive fluids from the NNSS. In the South African deep subsurface, *Desulforudis* is believed to utilize H_2 and SO_4^{2-} from radiochemical reactions; and until recently, this region was thought to define the geographic limit of the genus. Thus, the detection of *D. audaxviator* in radioactive subsurface water at the NNSS (up to about 6% of all bacteria by pyrotag analysis) was taken to support the inferred radiochemical lifestyle for *D. audaxviator*. More recently, however, our group has detected *Desulforudis* rRNA genes (*including near-perfect matches for D. audaxviator) in non-radioactive subsurface habitats on and near the NNSS; up to 1% of pyrotags in an 880 m-deep carbonate borehole near Death Valley, CA, for example. This observation, coupled with the fact that multiple bacterial and archaeal lineages appear to be shared between* deep NNSS/Death Valley boreholes and very deep habitats in South Africa, suggests that the truth is more complex.

Since our previous report, we have made a concerted effort to bring some of these cosmopolitan deep microbial lineages into cultivation with the aim of determining their effects upon the mobility of DOE legacy wastes (e.g. Pu) using laboratory microcosms. In particular, energy resources and dissolved gases representative of relevant habitats have been targeted. These efforts have resulted in viable (albeit to date non-transferable) colonies of *D. audaxviator. More robust cultivations of a variety of forms* first detected at great depth in African mines have also been achieved. These include sulfate-reducing Firmicutes, methanogens, and especially a locally-abundant group of Thaumarcheaota (e.g. SAGMA-14) that appear to grow anaerobically in pure culture by oxidizing methane or ammonia with sulfate as an electron acceptor. These results suggest that Earth may indeed possess a recognizable deep, hard rock microbiome and that understanding the nature of this little known realm of the microbial world may be necessary for predictive understanding of radionuclide mobility at some DOE sites.

NAME: Satish Myneni
ORGANIZATION: Princeton University
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Role of Sulfhydryl Sites on Bacterial Cell Walls in the Biosorption, Mobility and the Bioavailability of Mercury

ABSTRACT: Bacteria are ubiquitous in a wide-range of low temperature aqueous systems, and can strongly affect the distribution and transport of metals and radionuclides in the environment. However, the role of metal adsorption onto bacteria, via the reactive cell wall functional groups, has been largely overlooked. Previous macroscale metal sorption, and XAS studies have shown carboxyl and phosphoryl functional groups to be the important metal binding groups on bacterial cell envelops. However, our XAS studies have indicated that Hg^{2+} binds to sulfhydryl groups in preference to the more abundant carboxyl and phosphoryl groups on cell envelops when Hg concentration is submicromolar. The stoichiometry of these Hg-cysteine complexes on bacterial cell envelope changes as a function of the ratio of aqueous Hg concentration to bacterial cell density which has a significant impact on the solubility and bioavailability of Hg. The overall goal of our study is to provide a quantitative and mechanistic understanding of the impact of bacterial sulfhydryl groups on the uptake, speciation, transport and bioavailability of Hg in the environment.

We examined the speciation and stability of Hg complexes on the cell envelops of *Bacillus subtilis*, *Shewanella oneidensis* MR-1, and *Geobacter sulfurreducens* as a function of pH and aqueous Hg, in the presence and absence of organic (DOM) and inorganic (Cl^-) ligands. A novel technique using a fluophore was developed to characterize the concentration of reactive thiols on bacterial cell envelops. To complement fluorophore method, potentiometric titrations were performed after blocking the thiol sites. The estimated thiol density on the cell membranes of *B. subtilis* and *S. oneidensis* MR-1 obtained from these two different methods agrees well.

Hg XAS and UV-VIS luminescence spectroscopy studies indicate that Hg speciation is significantly different on methylating and non-methylating species. While the non-methylatig species (*S. oneidensis* MR-1 and *B. subtilis*) form the biologically unavailable HgS_3 (S= organic thiol) complex at low nanomolar Hg concentration, the methylating species *G. sulfurreducens* forms the bioavailable complexes HgS_2 (S = cysteine) at nanomolar Hg concentrations. Hg speciation on *G. sulfurreducens* was counter-intuitive because it exhibited HgS_2 complexes although it has far more reactive thiols on its cell envelope when compared to *S. oneidensis* MR-1. Transition from thiol to carboxyl binding occurred in the concentration range when all thiol sites on cell envelope were saturated.

We are currently exploring whether the presence of Hg induces thiol release onto the cell membranes or modify the redox behavior of reduced S-groups in the cell envelope, and the role of DOM on Hg interactions with different bacteria under different pH and DOM concentrations. We are also interested in understanding the ultimate fate of Hg complexed with cell envelope after cell turnover. Mercury is a common contaminant at several DOE sites, and our study provides important insights on the understanding of the bioavailaibilty, fate and transport of Hg at these sites.

NAME: Peggy O'Day
ORGANIZATION: University of California, Merced
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Molecular mechanisms and kinetics of microbial anaerobic nitrate-dependent U(IV) and Fe(II) oxidation

ABSTRACT: The stability and dissolution rate of solid U(IV)-oxide phases in aquifers are important for transport of dissolved U as the mobile uranyl cation ($U^{VI}O_2^{2+}$). Recent studies have suggested that microbially mediated, nitrate-dependent U(IV) oxidation under anaerobic conditions could complicate efforts at long-term reductive immobilization. We investigated the anaerobic, oxidative dissolution of biogenically produced U(IV)-oxide (nominally UO_2(s)) by either chemical oxidants (nitrate or nitrite) or by *Thiobacillus denitrificans*, a chemolitho-autotrophic bacterium that catalyzes anaerobic, nitrate-dependent U(IV) and Fe(II) oxidation. Mixtures of biogenic UO_2(s) and quartz with and without *T. denitrificans* were used in flow-through column experiments to examine coupled and competing oxidation-reduction processes. Abiotic oxidation of UO_2(s) in the presence of nitrate under anaerobic conditions was slow but faster than control experiments of non-oxidative dissolution. Abiotic UO_2(s) oxidation by nitrite was more rapid by several orders of magnitude. In the presence of *T. dentrificans* and dissolved nitrate, higher rates of dissolved U release were observed compared with abiotic controls, suggesting that *T. dentrificans* catalyzed the oxidative dissolution of UO_2(s) in addition to the abiotic oxidation pathways. X-ray spectroscopic characterization of reaction products indicated a fraction of solid-associated oxidized U(VI) that is retained in the column. Analysis of local atomic structures showed formation of U-oxo molecular moieties within or on particle surfaces that are similar but not identical to aqueous or sorbed uranyl species, suggesting mostly surface particle oxidation rather than detachment and re-adsorption of uranyl in the column. Reactive transport modeling (using Crunchflow) of column experiments incorporating thermodynamic solubility, irreversible overall abiotic and biotic kinetic reactions, and uranyl sorption on quartz was used to derive rates for overall kinetic reactions from column effluent U concentrations. Steady-state U concentrations were well simulated for a small amount of UO_2(s) oxidation relative to total UO_2(s) mass, but calculations were sensitive to particle surface area.

We investigated the enzymes involved in anaerobic, nitrate-dependent Fe(II) and U(IV) oxidation in *T. denitrificans*, as these enzymes have not yet been described for any other microorganisms that catalyze these processes. We previously reported that two *c*-type cytochromes, Tbd_0187 and Tbd_0146, were involved in anaerobic nitrate-dependent U(IV) oxidation in *T. denitrificans* and we hypothesized that *c*-type cytochromes would also catalyze nitrate-dependent Fe(II) oxidation. Studies to identify genes associated with nitrate-dependent Fe(II) oxidation included whole-genome transcriptional assays (including the use of $FeCO_3$, Fe^{2+}(aq), and U(IV) oxides as electron donors under denitrifying conditions), targeted insertion mutations of 26 genes of interest, and random transposon-mutagenesis studies with screening for Fe(II) oxidation. Non-defective mutants included the c_1-cytochrome subunit of the cytochrome bc_1 complex, which has relevance to a previously proposed role for this complex in nitrate-dependent Fe(II) oxidation. Of the transposon mutants defective in Fe(II) oxidation, one mutant with a disrupted gene associated with NADH:ubiquinone oxidoreductase (complex I) was >30% defective relative to the wild-type strain. Overall, our results indicate that nitrate-dependent Fe(II) oxidation in *T. denitrificans* is not catalyzed by the same *c*-type cytochromes involved in U(IV) oxidation, nor have other *c*-type cytochromes yet been implicated in the process.

NAME: Susan Pfiffner
ORGANIZATION: University of Tennessee, Knoxville
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Metaproteomics of Metal and Radionuclide Bioreduction

ABSTRACT: The project goal is to utilize innovative proteomics tools to generate new information regarding microbial activity contributing to metal and U(VI) reduction, and thus enable science-based decision making for long-term site management. Current objectives are to: (1) examine *c*-type cytochromes in *Anaeromyxobacter dehalogenans* strain 2CP-C, *Shewanella oneidensis* strain MR-1, and *Geobacter daltonii* strain FRC-32 under different growth conditions and develop a sequence library comprised of *c*-type cytochromes implicated in metal reduction and other redox processes; (2) examine the proteomes of these strains and identify proteins that correlate with metal reduction; and (3) apply proteomic analyses to ORIFRC field samples to demonstrate the utility of this approach for site assessment, efficient implementation of bioremediation and long-term monitoring. We used a tiered approach that combines database mining, controlled laboratory studies, and PCR approaches to support the proteomics characterizations.

c-Type cytochromes are heme-containing proteins involved in electron transfer to oxidized metal species. The genomes of *A. dehalogenans* strain 2CP-C, *S. oneidensis* strain MR-1, and *G. daltonii* strain FRC-32 encode 69, 40, and 72 *c*-type cytochromes, respectively. Distinct *c*-type cytochrome expression patterns were observed in cells grown with the different electron acceptors. Our proteome measurements revealed that the number of *c*-type cytochromes identified in Fe(III) and Mn(IV) grown cells were 19 and 20 (out of 40) for strain MR-1; and 27 and 25 (out of 69) for strain 2CP-C. Proteomic characterization of *c*-type cytochrome expression revealed substrate-dependent responses suggesting that c-type cytochrome profiling provides information about cellular metabolic activity.

To extend the proteome approach to field samples, proteomic analysis was performed on groundwater filters from Area 2 of the ORIFRC which were collected 4 days after the emulsified vegetable oil (EVO) amendment. The altered groundwater community in EVO amended well was dominated by members of the *Betaproteobacteria* (i.e., *Dechloromonas*, *Ralstonia*, *Rhodoferax, Polaromonas*, *Delftia, Chromobacterium)* and *Firmicutes*. When metaproteomic workflows were applied to early biostimulation (4 days after EVO injection), distinct differences in protein expression were observed between groundwater collected from wells up-gradient and down-gradient of the EVO injection gallery. In the biostimulated sample the prominent proteins were categorized as being proteins involved in ammonium assimilation, nitrous oxide reduction, EVO degradation, and polyhydroxybutyrate formation. *c*-Type cytochromes and citrate synthase, which is a biomarker for hexavalent uranium reduction activity, were detected in low abundances suggesting that metal reduction has not commenced 4 days following EVO injection. Thus environmental metaproteomics provided valuable information and complemented nucleic acid-based approaches for identifying microbial community responses to biostimulation and elucidating active metabolic pathways.

NAME: Brian Powell
ORGANIZATION: Clemson University
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Development of a Self-Consistent Model of Plutonium Sorption: Quantification of Sorption Enthalpy and Ligand-Promoted Dissolution

ABSTRACT: The overarching objective of this work is to examine Pu(IV) and Pu(V) sorption to pure metal (oxyhydr)oxide minerals and sediments using variable temperature batch sorption, X-ray absorption spectroscopy, electron microscopy, and quantum-mechanical and empirical-potential calculations. The data will be compiled into a self-consistent surface complexation model. The novelty of this effort lies largely in the manner in which the information from these measurements and calculations will be combined into a model that will be used to evaluate the thermodynamics of Pu sorption reactions as well as to predict sorption of Pu to sediments from DOE sites using a component additivity approach. This study has demonstrated that sorption of Pu cannot be simply described by interactions between a single oxidation state. Rather the complex, redox sensitive nature of Pu must be fully constrained in order to obtain a sorption model which accurately predicts the observed species. This presentation will focus on the progress made in the past year examining 1) quantification of actinide sorption enthalpies, 2) examination of the mechanisms underlying surface mediated redox reactions, and 3) aging of Pu surface complexes resulting in irreversible or hysteretic sorption.

Quantification of actinide sorption enthalpies: The sorption of Eu(III), Np(V), Pu(IV), and Pu(V) to the iron oxide minerals hematite and goethite has been examined as a function of temperature. Quantifying the sorption constants allows for evaluation of the sorption enthalpy and entropy through the use of a van't Hoff plot. Both Eu(III) sorption to hematite and Pu(IV) sorption to goethite had positive enthalpy values and entropy values. These measurements are consistent with the experimental hypothesis that removal of hydrating waters provides an entropically driven free energy of these sorption reactions. The entropy of Eu(III) and Pu(IV) were $439 \pm 26\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ and $187 \pm 25\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, respectively. The higher value for Eu(III) indicates the importance of the loss of at least 5 of the initial 9 hydrating water molecules upon sorption. This loss of water upon sorption and formation of a bidentate surface complex was verified using quantum mechanical modeling, extended x-ray absorption fine structure spectroscopy (EXAFS), and electron microscopy. The surface complexation models generated as part of this task have been used to successfully predict successfully sorption of Np(V) and Pu(IV/V) to Hanford 200 Area sediments.

Examination of surface mediated reduction: Using quantum mechanical modeling and dual isotope batch sorption experiments, a series of experiments has examined the reduction of Pu(V) to Pu(IV) on mineral surfaces. These experiments are vital to understanding the frequent observations of surface mediated Pu(V) reduction on non-redox active mineral surfaces such as quartz (which was verified in this work using X-ray absorption near edge structure spectroscopy, XANES). Dual isotope batch sorption tests using ^{242}Pu and ^{238}Pu demonstrated that processes such as generation of radiolytic byproducts of water and disproportionation of Pu at the surface were unlikely to be the cause of Pu(V) reduction. These results were supported by quantum mechanical modeling which examined the influence of various radiolytic byproducts which were co-adsorbed with Pu.

Aging of Pu surface complexes: Desorption of $^{239/240}$Pu was examined on a subsurface sediment from the Savannah River Site which had been aged 32 years. To compare the aged Pu with "fresh" Pu, ^{242}Pu was reacted with the aged Pu-contaminated soils for three days. Batch sorption/desorption experiments and selective extractions for total and amorphous iron demonstrated that the reversibility of sorption of Pu decreases significantly with aging time. This may be due to the transfer of Pu from amorphous to crystalline iron phases within the soil matrix or stronger binding of Pu to the solid surface based on the dehydration of the surface complex as described above.

NAME: Harihar Rajaram
ORGANIZATION: University of Colorado, Boulder
PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Scale-Dependent Fracture-Matrix Interactions And Their Impact on Radionuclide Transport

ABSTRACT: Matrix Diffusion and Adsorption within a rock matrix are important mechanisms for retarding transport of radionuclides in fractured rock. Due to computational limitations and difficulties in characterizing complex subsurface systems, diffusive exchange between a fracture network and surrounding rock matrix is often modeled using simplified conceptual representations. There is significant uncertainty in "effective" parameters used in these models, such as the "effective matrix diffusivity". Often, these parameters are estimated by fitting sparse breakthrough data, and estimated values fall outside meaningful ranges, because simplified interpretive models do not consider complex three-dimensional flow. There is limited understanding of the relationship between the effective parameters and rock mass characteristics including network structure and matrix properties. There is also evidence for an apparent scale-dependence in "effective matrix diffusion" coefficients. These observations raise questions on whether fracture-matrix interaction parameters estimated from small-scale tracer tests can be used for predicting radionuclide fate and transport at the scale of DOE field sites.

High-resolution three-dimensional Discrete-Fracture-Network-Matrix (DFNM) models based on well-defined local scale transport equations can help to address some of these questions. Due to tremendous advances in computational technology over the last 10 years, DFNM modeling in relatively large domains is now feasible. The overarching objective of our research is to use DFNM modeling to improve fundamental understanding of how effective parameters in conceptual models are related to fracture network structure and matrix properties. An advanced three-dimensional DFNM model is being developed, which combines upscaled particle-tracking algorithms for fracture-matrix interaction and a parallel fracture-network flow simulator. The particle-tracking algorithms allow complexity in flow fields at different scales, and track transport across fracture-matrix interfaces based on rigorous local approximations to the transport equations. This modeling approach can incorporate aperture variability, multi-scale preferential flow and matrix heterogeneity. The code can handle computational domains with about 1 Billion nodes for flow and 1 Billion particles for transport. The overarching goal is to obtain insights on (i) the relationship between effective fracture-matrix interaction parameters, network structure and matrix properties and (ii) their scale dependence in different types of fractured rock environments.

We will present results obtained using "high-resolution" particle tracking algorithms in large-scale (~10,000 fracture) fracture networks in which small-scale aperture variability is explicitly represented within each fracture. Flow simulations in these fracture networks illustrate the important role of head variations along an intersection in driving flow through slow advective loops in dead-end fractures. Subsequent transport simulations demonstrate that these advective loops lead to long-tailed breakthrough curves even in the absence of true matrix diffusion. Ongoing efforts are focused on extending the network flow and transport simulations to very large scales by including recently developed "upscaled" particle-tracking algorithms, which allow use of much larger time steps. The

upscaled algorithms have been verified using the “very-high-resolution” simulation results as a benchmark, and hold significant promise as an efficient tool for field-scale simulation.

The final stage of our research will specifically target applications at the Oak Ridge Field Research Center, former nuclear test sites in Nevada (e.g. the Shoal and Bullion tests), and other field sites (e.g. Mirror Lake) where tracer tests were conducted to obtain fracture-matrix interaction parameters for site-scale transport models. We will explain the differences in behavior observed at these sites using our network model and subsequently simulate radionuclide transport at the site scale and 100+ year time scales.

NAME: Peter H. Santschi
ORGANIZATION: Texas A&M University - Galveston
PROGRAM AFFILIATION: SBR

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

ABSTRACT: 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 [**1,2**]. 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}I/^{127}I) and speciate I via GC-MS **[3].** Results using this new method demonstrate that the mobility of ^{129}I species greatly depends on the type of I species and its concentration **[4,5],** pH **[6,7],** and sediment redox state **[7],** with equilibration times taking up to 12 weeks [**6,7**]. For example, at ambient concentrations (~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 **[5].** Iodate removal can also occur through incorporation into $CaCO_3$ crystal lattice, e.g., at the Hanford Site [**8**]. Iodide and iodate interactions with NOM leads to covalent binding of I to a limited number of aromatic carbon moieties on the particle surface [**6,9,10,11].** Iodine association with NOM is important in sediments, even when organic carbon are very low (e.g., <0.2% at Hanford Site) [**8,12**]. Removal of iodine from the groundwater through interaction with NOM is complicated by the release of mobile organo-I species **[9,10,11].** A small fraction of NOM that is bound to iodine can behave as a mobile organo-I source **[9],** a process that we were able to numerically simulate using kinetic Michaelis-Menton-type redox-reactions and kinetic uptake reactions [**2**]. Field [**13**] 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 SRS indicate that an increase of 0.7 pH units in groundwater over 17 years may explain the observed increased groundwater ^{129}I concentrations [**14**]. Bacteria from a ^{129}I-contaminated aerobic aquifer at the F-area of SRS can accumulate I$^-$ at environmentally relevant concentrations (10^{-7} M), but account for only a minor fraction of total added iodide (0.2-2.0%) **[15],** indicating that bacterial I$^-$ accumulation likely does not account for the high fraction (up to 25% of total I) of measured organo-I in groundwater [**4,16**]. However, enzymatic oxidation of I$^-$ likely plays a greater role in iodination of NOM, and is currently being investigated further **[15,17].** Iodide oxidizing activity of bacteria and organic acid produced by bacteria significantly contribute to organo-iodine formation **[15,17]. Our references: [1]** Kaplan et al. 2013. Crit. Rev. Environ. Sci. Technol., subm. **[2]** Chang et al. 2013. ES&T, subm. **[3]** Zhang et al. 2010. ES&T*,* 44, 9042. **[4]** Schwehr et al. 2009. ES&T 43, 7258. **[5]** Zhang et al. 2011. ES&T 45, 5543. [**6**] Xu et al. 2011. ES&T 45, 9975. [**7**] Emerson et al. 2013. Chem. Geol., subm. [**8**] Zhang et al. 2013. ES&T, in subm. [**9**] Xu et al. 2011. GCA 75, 5716. [**10**] Xu et al., 2013. STOTEN 449, 244. [**11**] Xu et al. 2012. GCA 97, 166. [**12**] Xu et al., 2013. ES&T, in subm. [**13**] Otosaka et al. 2011. STOTEN 409, 3857. [**14**] Kaplan et al. 2011. ES&T 45, 489. **[15]** Li et al. 2011. *Appl. Environ. Microbiol.* 77, 2153. [**16**] Li et al. 2012. p. 89-97. In: *Interdisc. Stud. Environ. Chem. Vol. 6 - Environ Poll. Ecotox. Terra Sc. Publ. Comp. Tokyo*. [**17**] Li et al. 2012. ES&T 46, 4837.

NAME: Peter H. Santschi
ORGANIZATION: Texas A&M University - Galveston
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Plutonium Immobilization and Re-mobilization by Soil Mineral-Organic Matter Matrix Compounds

ABSTRACT: 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}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 [2,3]. The role of NOM in both immobilizing or re-mobilizing Pu thus has been demonstrated. It was found that partitioning coefficients (K_d) of intact humic acids (HAs) were sigificantly higher than those when HA was treated with HF, due to a lower number of chelating sites for Pu in the HF-treated HAs, or due to hydrophobicity differences between the two types of HAs. K_ds of Pu (IV) with HAs were higher at low pH (4.4) than those at high pH (7.1), in contrast to the observation of Pu sorption to most mineral phases [4], possibly caused by the increased solubility of HA under more alkaline conditions. Though the colloidal fraction of HAs (>1kDa MWCO) only accounts for a minor fraction of total OC (<5%) at pH 4.4, Pu binding to HAs accounts for 61-83% of the total added Pu, indicating that colloidal organic matter is the mobile Pu carrier in the wetland area. Lastly, ^{239,240}Pu concentrations were found to be positively correlated to particulate hydroxamate and nitrogen contents, demonstrating Pu binding to siderophores, a NOM compound. Additional research involves the extraction and synthesis of the NOM precursor of the organic Pu carrier. In a previous study, almost all of the mobile ^{239,240}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 moeties such as polysaccharides (to increase its solubility and thus mobility), hydroxamate (one type of siderophore compounds), and amide functionalities (both to chelate iron and Pu) [3]. To help understand Pu interactions with cutin and siderophore degradation products, a modified method [5] was used to extract the cuticle material from Western wheatgrass (*Agropythi Smithii*), one of the dominant vegetation species at the RFETS. The crude cuticle extract contains a significant portion of residual carbohydrates and amide functionalities. This cutin material was further purified to remove carbohydrates. Oxidation experiments were carried out to investigate the depolymerization of cutin, incoporation of carbohydrates, siderophore compounds, as well as the chelation of iron(III) (as a surrogate of Pu(IV)) during a simulated humification process. Finally, using advanced analytical tools to quantify and identify NOM moities (^{13}C NMR, HRMAS, ATR-FTIR, etc.), this material was compared with the naturally-occuring organic colloidal Pu carrier [3] to unravel the history of the molecular basis for the Pu vector in the enviroment.. **References:** [1] Kaplan et al. (2007), *ES&T* 41, 7417-7423. [2] Santschi et al. *ES&T* 36, 3711-3719. (2002). [3] Xu et al. (2008) *ES&T* 42, 8211-8217. [4] Kaplan et al. (2006), *ES&T* 40, 5937-5942. [5] Deshmukh et al. (2003) *Phytochemistry* 64, 1163-1170.

NAME: Michelle Scherer

ORGANIZATION: University of Iowa

PROGRAM AFFILIATION: SBR

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

ABSTRACT: 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.
3. Assess whether Fe(II)-Fe(III)$_{clay}$ electron transfer and atom exchange will impact the redox cycling of U and inorganic Hg in the subsurface.

Our findings indicate that electron transfer occurs between sorbed Fe(II) and structural Fe(III) in two well-characterized smectites (NAu-1 and NAu-2). More specifically, our findings demonstrate that electron transfer to structural Fe in clay minerals can occur from Fe(II) sorbed to both basal planes and edge OH-groups. We used Mössbauer spectroscopy with selective chemical extractions to distinguish electron transfer from Fe(II) sorbed to basal planes and to edge OH-groups and observed more extensive electron transfer from edge OH-groups at pH value 7.5 compared to electron transfer from basal plane-sorbed Fe(II) at pH 4.0 and 6.0. Interestingly, the Mössbauer hyperfine parameters for the reduced structural Fe(II) in the clay mineral were distinctly different depending on whether reduction occurred from Fe(II) sorbed to basal planes or edge-OH groups. Preliminary data suggest that electron transfer results in exchange of Fe atoms between the aqueous phase and clay mineral structure as we have previously observed for Fe(III) oxides. Continuing work is underway combining enriched-57Fe tracers with monitoring natural, mass-dependent stable Fe isotope fractionation via 56Fe/54Fe to evaluate both the mechanism of atom exchange and and whether Fe atom exchange may be accompanied by significant stable Fe isotope fractionation.

We also applied first principles calculations using a small polaron hopping approach and Marcus electron transfer theory to examine electron exchange mobilities in a smectite clay mineral. Our calculations provide rates of electron hopping that agree very well with values deduced from variable temperature Mössbauer data indicating a surprisingly fast electron mobility at room temperature and suggest that electron hopping within the octahedral sheet should dominant.

NAME: Jonathan (Josh) Sharp
ORGANIZATION: Colorado School of Mines
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Coupled biogeochemical exploration of contaminant mobility at the microbe / mineral interface

ABSTRACT: Concurrent arsenic mobilization to levels as high as 9 µM at the U.S. Department of Energy's Integrated Field Research Challenge (IFRC) site in Rifle, Colorado highlights one of the challenges to widespread use of biostimulation for uranium immobilization. The addition of acetate to this shallow alluvial aquifer results in a shift from iron to sulfate reducing conditions. Arsenic release correlates with sulfate reduction and is characterized by a dominance of soluble arsenic-sulfur species (thioarsenics). To further explore this phenomenon, laboratory sediment columns derived from the site were seeded with *Geobacter sulfurreducens* and fed a synthetic groundwater containing 19 ± 2 mM acetate for ~135 days. After achieving iron-reducing conditions, columns were differentiated by three treatments: high sulfate (10 mM SO_4^{2-}), low sulfate (1mM SO_4^{2-}) and inhibition of sulfate reduction (10mM SO_4^{2-} + 1.5 mM molybdate). The 'high sulfate' column is most analogous to field conditions at the Rifle IFRC, which had 8-10 mM SO_4^{2-} in groundwater pre- and post-stimulation. In each case, column effluent showed an initial increase in soluble arsenic to approximately 1 µM, presumably associated with reductive dissolution of Fe- and Mn- solids, followed by a slow decline over the remainder of the experiment. While significant quantities of thioarsenic species could be formed in the laboratory by combining sulfide and arsenite at circumneutral pH in aqueous batch, arsenic breakthrough in the three flow through-columns was independent of sulfate-reduction. Similarly low concentrations of thioarsenics formed in the high sulfate, low sulfate and the sulfate-reduction-inhibition column which, by the end of the experiment, were evolving ~8,000 µM, ~300 µM, and ~10 µM sulfide, respectively. For comparison, sulfide concentrations reached ~300 µM in the field during peak sulfate reduction. Furthermore, the introduction of a pulse of soluble As(III) to the columns resulted in >85% of total arsenic being immobilized, presumably due to sorption or formation of FeS species, rather than significant thioarsenic evolution. Analysis of the microbial community by 16S rRNA gene 454 pyrosequencing indicates dominance by the orders of Clostridiales, Rhodospirillales, Burkholderiales, and Pseudomonadales with *C. delftia* as the most prevalent species. To further deconstruct the role of different microorganisms and geochemical conditions in these flow-through systems, work is transitioning to the mineral-microbe interface using sediment and mineral thin section (~60 um) coupons sorbed with As(V). By colonizing the coupons with axenic bacteria that are selected for iron, sulfate and arsenic respiratory processes, we can monitor for alterations in geochemical and biofilm properties associated with microbial colonization. Through ongoing biofilm visualization development pairing fluorescence *in situ* hybridization (FISH) with quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN) new possibilities for visualizing these types of microbe-metal interactions is evolving. In addition a protocol for species-specific metallo-labeling of microbial cells for subsequent SEM and synchrotron-based micro-XAS analysis is currently being optimized in order to concurrently monitor elemental redox, mineralogical associations and microbial processes at the micron scale. This novel approach exploits the versatility and cost-efficiency of *in situ* hybridization-based methods without the limitations of fluorescence-based detection of cells in complex environmental samples. Collectively this work has importance in merging existing molecular and geochemical toolsets to investigate complex mineral-microbe processes relevant to metal fate and transport.

NAME: Jeremy Smith

ORGANIZATION: University of Tennessee, Knoxville

PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Basis for Strong Affinity of Mercury for Soft Ligands and Computational Studies of Mercuric Reductase (MerA) Mechanism

ABSTRACT: Mercury's preference for soft ligands such as thiols has been conceptualized in the theory of hard and soft acids and bases (HSAB), i.e. hard (less polarizable) metals have higher affinities for hard ligands than for soft (more polarizable) ligands, and vice versa. We have made the surprising finding that absolute affinities of Hg2+ for two anionic ligands (L-) computed in the gas phase trend in the opposite direction to those affinities computed in water. That is, the gas-phase free energy of forming HgL2 becomes more favorable with ligand hardness. In contrast, the aqueous-phase Hg2+ affinity increases with ligand softness. This switch in affinity upon hydration becomes apparent on addition of as few as two explicit water molecules and is obtained within both the chalcogenide and halide groups, in agreement with the long observed preference of Hg2+ for soft ligands in aqueous solution. Moreover, by comparing binding of one versus two anions to Hg2+, we found that the gas-phase trend for forming HgL2 arises from the enhanced reactivity of HgL+-. Our approach establishes a quantitative theoretical basis for predicting Hg speciation in the biosphere.

Mercuric reductase, MerA, the key enzyme in the bacterial mercury resistance (*mer*) system, catalyzes the NADPH-dependent reduction of mercuric ion, Hg2+, to elemental Hg0. Each of the two monomers of the MerA homodimer contains a flavin adenine dinucleotide (FAD) cofactor that mediates electron transfer from NADPH to Hg2+ bound to the inner pair of cysteines in the active site (C136/C141 of *Pseudomonas aeruginosa* Tn*501* MerA numbering). A second cysteine pair at the C-terminus of the other monomer (C558’/C559’) is essential for acquiring and transferring Hg2+ to the inner pair. Here, quantum mechanical/molecular mechanical (QM/MM) simulations elucidate the steps of MerA reduction, (a) equilibration between two redox states of the cofactors, NADPH/FAD and NADP+/FADH-, (b) Hg2+-transfer from the outer C-terminal cysteine pair to the inner active site cysteine pair, and (c) the reduction of the C136-C141 disulfide and the C136-S-Hg-S-C141 complex by FADH-, the two-electron reduced FAD. This analysis establishes the first atomic-level, energetic description of the MerA mechanism and contributes generally to understanding intracellular metal trafficking and catalysis by the larger family of NAD(P)-dependent flavin-disulfide oxidoreductases.

NAME: Robert Smith

ORGANIZATION: University of Idaho

PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Persistence of Microbially Facilitated Calcite Precipitation as an in situ Treatment for Strontium-90 and Other Metal Contaminant

ABSTRACT: Subsurface radionuclide and metal contaminants throughout the U.S. Department of Energy (DOE) complex pose one of DOE's greatest challenges for long-term stewardship. One promising stabilization mechanism for divalent ions, such as the short-lived radionuclide ^{90}Sr, is co-precipitation in calcite. We have previously found that nutrient addition can stimulate microbial ureolytic activity, that this activity accelerates calcite precipitation and co-precipitation of Sr, and that higher calcite precipitation rates can result in increased Sr partitioning. We have conducted integrated field, laboratory, and computational research to evaluate the relationships between ureolysis and calcite precipitation rates and trace metal partitioning under environmentally relevant conditions, and investigated the coupling between flow/flux manipulations and precipitate distribution.

A field experimental campaign conducted at the Integrated Field Research Challenge (IFRC) site located at Rifle, CO was based on a continuous recirculation design; water extracted from a down-gradient well was amended with urea and molasses (a carbon and electron donor) and re-injected into an up-gradient well. The goal of the recirculation design and simultaneous injection of urea and molasses was to uniformly accelerate the hydrolysis of urea and calcite precipitation over the entire inter-wellbore zone. The urea-molasses recirculation phase lasted, with brief interruptions for geophysical surveys, for 12 days followed by long-term monitoring which continued for 13 months. Following the recirculation phase we found persistent increases in urease activity (as determined from ^{14}C labeled laboratory urea hydrolysis rates) in the upper portion of the inter-wellbore zone. We also observed an initial (first 2 weeks) increase in urea concentration associated with injection activities. After injection ceased, we observed a decreased urea concentration and increased in ammonium and dissolved inorganic carbon (DIC). Based on the loss of urea and the appearance of ammonium, a first order rate constant for urea hydrolysis of 0.18 day^{-1} and an associated R_f value for ammonium of 11 were estimated. The rate constant is approximately 6 times higher than estimated for previous field experiments conducted in eastern Idaho. Additionally, DIC carbon isotope ratios were measured for the groundwater. Injected urea had a δ^{13}C of -40.7±0.4 ‰ compared to the background groundwater DIC δ^{13}C of -16.6±0.2‰. Observed decreases in groundwater DIC δ^{13}C of up to -19.8‰ followed temporal trends similar to those observed for ammonium and suggest that both the increase in ammonium and the shift in δ^{13}C are the result of urea hydrolysis.

Analysis of a conservative tracer test conducted one year after the end of recirculation and comparison with a pre-injection tracer test indicated that the urea and molasses amendment resulted in preferential blocking of flow access to lower permeability zones and consequent flow focusing within the most conductive portion of the aquifer. Additionally, exchangeable ammonium was observed in the lower portion of the post-injection core. Although direct observation of calcite precipitation was not possible because of the high pre-existing calcite content in the site sediments, an observed δ^{13}C decrease for solid carbonates from sediment samples collected following urea injection (compared to pre-injection values) is likely the result of the incorporation of inorganic carbon derived from urea hydrolysis into newly formed solid carbonates.

NAME: Patricia Sobecky
ORGANIZATION: University of Alabama
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Uranium Biomineralization by Natural Microbial Phosphatase Activities in the Subsurface

ABSTRACT: The main objective of this project is to examine the role of phosphohydrolases in naturally occurring subsurface bacteria for the purpose of promoting the immobilization of uranium through the formation of insoluble uranium phosphate minerals. Our prior work focused on pure culture and soil column studies that utilized contaminated soils from the DOE Oak Ridge Field Research Center (ORFRC) to demonstrate that microbial phosphatase activity liberated enough inorganic phosphate (PO_4^{3-}) from synthetic organophosphate compounds to promote uranium-phosphate mineral formation under oxic and anoxic conditions at different pH (pH 5.5 and 7). Simultaneously, addition of exogenous organophosphate was shown to promote the formation of intracellular polyphosphate. The objective of the present research was to examine the potential of utilizing phytate, a naturally-occurring and abundant organophosphate in soils, as a phosphorous source to promote U(VI)-phosphate biomineralization by natural microbial communities. While phytate hydrolysis in aerobic incubations of ORFRC soils was not evidenced at pH 7.0, complete hydrolysis was observed both with and without electron donor at pH 5.5, suggesting indigenous microorganisms express acidic phytases in these soils. The presence of uranium accelerated phytate hydrolysis but decreased the rate of hydrolysis of inositol intermediates as a result of a possible toxicity effect on the indigenous population. The abundant production of inorganic phosphate drastically decreased uranium solubility via formation of ternary sorption complexes and precipitation of U(VI)-phosphate minerals. Two phytase-positive microorganisms identified as *Bradyrhizobium* and *Variovorax* species by 16S rRNA sequencing were isolated from these soils. To determine the effect of uranium on phytate hydrolysis by ORFRC microorganisms, *Variovorax* sp. was exposed to increasing concentrations of uranium then incubated aerobically in pH 5.5 artificial groundwater amended with an electron donor and phytate as the sole phosphorus source. The hydrolysis of phytate by cells exposed to uranium was incomplete compared to unexposed cells, yet cells grew even in the presence of elevated uranium concentrations. Simultaneously, total inorganic phosphate production decreased linearly with increasing uranium concentrations, indicating a significant uranium toxicity effect on the cells. More importantly, exposure to increasing uranium concentrations resulted in earlier onset and more rapid accumulation of inorganic phosphate compared to identical reactors without uranium, suggesting phytate hydrolysis is activated as a uranium detoxification mechanism. Overall, the results of this study demonstrate the ability of natural microbial communities to liberate phosphate from phytate in acidic soils and the potential utility of phytate-promoted biomineralization of U(VI)-phosphate minerals as a uranium immobilization strategy.

NAME: Anne Summers
ORGANIZATION: University of Georgia
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Defining the Molecular-Cellular-Field Continuum of Hg Detoxification

ABSTRACT: Very effective Hg detoxifying proteins have evolved in many bacteria and archaea. Exploiting removal of Hg^{2+}/$MeHg^{+}$ in wetlands by such naturally Hg resistant (HgR) bacteria requires knowing how these proteins work. We study HgR genes of α- and γ -proteobacteria and actinobacteria abundant in the ORR and report here on the mechanisms of the *mer* reductase (MerA) and demethylase (MerB) and regulatory proteins that optimize their expression. We also report on novel specific, high affinity Hg binding to natural, cellular nucleic acids.

ʰπPROTEOBACTERIAL FUSED MerB-MerA: *Ochrobactrum anthropi*, a relative of α-proteobacteria found in the East Fork Poplar Creek, have a *merBmerA* gene encoding a novel fused MerB-MerA with demethylase and *mer* reductase activities. We cloned the full fusion and its separate *merB* and *merA* genes and properties of all three constructs will be presented.

ɹπPROTEOBACTERIAL MerA: Reduction of Hg^{2+} in all MerA proteins occurs deep within the catalytic domain. Two cysteines near the C-terminus transfer Hg^{2+} from dithiol complexes in solution to a pair of cysteines in the active site. Altered rates for Hg^{2+} acquisition and reduction with a K449A mutation suggest K449 electrostatically controls dynamic motions of the C-terminal tail. Computational studies implicate two additional residues. Effects of mutations of these on kinetic and dynamic properties of the enzyme will be presented.

ACTINOBACTERIAL MerA/MerB: Relatives of *Streptomyces lividans* are also found in high Hg regions of the ORR. *S. lividans* MerA lacks the tethered NmerA domain found in γ -proteobacterial MerA, and its MerB lacks a cysteine of proteobacterial MerB essential for Hg^{2+} transfer to NmerA, but has a distinct C-terminal cysteine pair whose role in RHg^{+} binding and Hg^{2+} release is being probed by mutagenesis.

Hg ISOTOPE FRACTIONATION BY PURIFIED MerA: Distinct signatures in Hg isotope fractionation are important for distinguishing biotic and abiotic contributions to natural Hg cycling. Kritee et al (2007) measured Hg isotope fractionation by intact cells expressing *mer* genes and proposed that MerA is largely responsible for the observed effects. To test this in vitro, we're measuring Hg isotope fractionation with a purified γ-proteobacterial MerA. Technical challenges and progress will be presented.

PROTEOBACTERIAL REGULATION OF *mer* EXPRESSION: In gamma-proteobacteria, repressor-activator MerR holds RNA polymerase (RNAP) at the *mer* operator-promoter (MerOP) until Hg^{2+} stimulates it to let RNAP transcribe. We find that Hg^{2+} also binds the 38 bp MerOP DNA in the absence of thiols (as in acute Hg^{2+} exposure) at 2-3 high affinity sites. The EXAFS spectrum of Hg-MerOP is indistinguishable from pure thymidine(T)+Hg and best fits two N ligands. Calorimetry reports similar high affinity sites in the upper and lower MerOP single strands and in the Hg + T interaction. Once formed, Hg-DNA adducts are only slowly removed by a two-fold excess of cysteine. T's do not abut in B-form DNA, but MerOP may adopt a cruciform structure where two Ts abut in the lower strand loop and we are currently testing relevant mutants. Intact *E.coli* cells bind >3-fold more Hg^{2+} than their available thiols could bind and EXAFS indicated N or O ligands are involved. MerOP-Hg binding reveals Hg binding distinct from the classic model based on slippage in AT runs, so DNA and RNA (uracil) may be an unrealized sink for Hg^{2+}

with unknown turnover. We are pursuing this broader aspect of Hg biology with larger defined DNA and RNA molecules.

ACTINOBACTERIAL REGULATION OF *mer* EXPRESSION: In contrast, Actinobacteria control the *mer* operon with a simple ArsR-type repressor. The *S. lividans* MerR (SLMerR) is a distinct clade of the ArsR family which, by homology, shows a possible Hg^{2+} binding site near its DNA recognition helix, very different from metal sites in other ArsR regulators. SLMerR over-expression was toxic in *E.coli* due to codon incompatibility, so we synthesized a codon-optimized *S.lividans merR* gene with a His-tagged SUMO fusion for facile purification of a tagless wildtype protein. This has worked beautifully with 100% cleavage yielding completely pure, soluble SLMerR at approximately 12-13 mg/L, ready to scale up for biochemical and biophysical studies.

NAME: Anne Summers
ORGANIZATION: University of Georgia
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Identifying Components of Toxic Metal Stress and Hg Methylation with Global Proteomics

ABSTRACT: Methylmercury (MeHg) and inorganic Hg directly inactivate proteins by binding to their cysteine or selenocysteine residues. As recently reported (Polacco, et al. MCP, 2011), we have devised a high-throughput global proteomics method using the 7 stable isotopes of Hg to identify proteins of *E.coli* most vulnerable to forming stable adducts of phenylmercury (PhHg; a proxy for methylmercury) and are now also using this proteomics method to identify proteins involved in Hg methylation by *Desulfovibrio* ND132. The *E.coli* dataset of ~1.62 million total observed MS2 spectra from three complete biological replicates identified 1562 of *E.coli* MG1655's 4249 encoded proteins (37% of total) and 303 of these, in a wide variety of functional groups, had stable cysteine-Hg adducts (Zink et al, in preparation). Bulk cell properties altered by PhHg or Hg exposure include thiol homeostasis, electrolyte balance, and free iron (LaVoie et al, in preparation).

PROTEOMIC LABEL-FREE QUANTIFICATION OF Hg PEPTIDES – Quantification of unique modified peptides can afford comparison of their relative detectability as a function of different iodoacetamide (IAM) treatments after phenylmercury acetate (PMA) exposure. We devised an indirect and a direct method for quantifying peptides modified by PMA. First, since existing signal collation methods are challenged by the 7 stable isotopes of Hg, we simply used current label-free AMT methods to quantify indirectly the PMA-provoked decline in iodoacetylation modifications (CAM-mods) of 428 robustly observed peptide cysteines. PMA-exposure decreased CAM-mods in essentially all detectable cysteines by ~5-fold (average). This PMA-provoked decrease per-cysteine was sufficiently reproducible to allow ranking each cysteine for likelihood of PhHg modification. Our second approach to quantifying Hg-modified peptide cysteines was achieved by a novel computational breakthrough in LC-MS feature detection allowing use of the broad isotope envelopes of Hg peptides and, thereby, the direct quantification of 369 Hg-modifed peptide cysteines. With this latter tool we found Hg-modified peptides decreased in cells treated with 20 mM IAM but not with 10 mM IAM (vs. no IAM treatment) but in this case the decrease was only 1.7-fold, a difference too small to rank cysteines as more or less likely to suffer an Hg-adduct. While it is not yet clear why the indirect metric of CAM-mods per peptide cysteine display a wider range than the direct measure of the Hg-mods themselves, this latter new method will greatly expedite robust direct assessment of the modifiability of individual peptide cysteines.

STABILITY OF Hg-PEPTIDES TO PROTEOMICS: We find the abundance of Hg-modifiable peptides is lower than their unmodified form and the same is true of the Hg-modified tripeptide, glutathione (GSH). Possible technical factors include differential stability to pre-column procedures, column conditions, and MS conditions. Initial experiments with a pure Hg-adduct peptide showed it was stable to a broad range of MS inlet temperature and voltage conditions. We are extending this analysis to a more hydrophobic peptide and additional work with Hg- and CAM-modified GSH and lysozyme.

Hg EXPOSOME OF A METHYLATING BACTERIUM: To identify proteins involved in Hg^{2+} uptake and methylation we have first done a total proteome on *Desulfovibrio* ND132 growing facultatively without Hg^{2+} to test the efficacy of our modified proteomics method on it. We saw 3008 proteins of 3455 encoded (87%; based on 66,121 distinct peptides) considerably more than reported on pyruvate or fumarate grown *Desulfovibrio* G20 (1900 identified proteins of 3258 encoded), likely due to better recovery of cysteine-containing peptides with IAM treatment. Indeed, we observed 1851 cysteine-containing proteins of 3071 encoded (60%). Preliminary analysis of an Hg-exposed ND132 proteome done with and without IAM treatment yielded 28,622 distinct peptides corresponding to just 2,535 proteins. Of these, 3,921 distinct peptides were modified with CAM and 308 with Hg. Differences with respect to the no-Hg ND132 proteome and with respect to the *E.coli* PMA-exposure proteome will be discussed. In related work, a double mutant in the genes (*hgcAB*) encoding the newly discovered Hg(II) transmethylase is only slightly less resistant to Hg(II) than its parent wild-type strain, showing definitively that the ability to methylate Hg does not enhance resistance to Hg, as had been earlier suggested by work with unrelated methylating and non-methylating field isolates of *Desulfovibrio.*

NAME: Martial Taillefert
ORGANIZATION: Georgia Institute of Technology
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Mineral Solubility and Free Energy Controls on Microbial Reaction Kinetics: Application to Contaminant Transport in the Subsurface

ABSTRACT: Recent developments in the theoretical treatment of geomicrobial reaction processes have resulted in the formulation of kinetic models that directly link the rates of microbial respiration and growth to the corresponding thermodynamic driving forces. In this project, these kinetic models for the microbial reduction of uranium(VI) are verified and calibrated. The approach combines laboratory experiments on uranium bioreduction using pure cultures and natural samples, competition between reduction of U(VI) and iron oxides, and field-scale reactive transport modeling. Gibbs free energy yields are manipulated by varying the concentrations of U(VI), type and concentration of iron oxides, electron donor, as well as the carbonate alkalinity, and calcium concentrations. Rates of enzymatic reduction of U(VI) were measured under variable, but controlled, geochemical conditions to determine the effect of pH on bioreduction rates by *Shewanella putrefaciens*. In the presence of excess carbonates, the pH decreased over time prompting a shift in U(VI) speciation from U(VI)-carbonato complexes toward more readily-reducible U(VI)-hydroxide and increased bioreduction rates. Ca^{2+} suppressed the formation of labile U(VI) complexes and required a larger decrease in pH to achieve comparable rates. These results indicate that the main reducible fraction of U(VI) consists of hydroxide complexes, despite being the least abundant species in solution, and suggest that the pH decrease associated with U(IV) precipitation is required to promote U(VI) bioreduction in the presence of carbonates and calcium. If the pH is too low, however, it may have a toxic effect on cells. Experiments conducted at pH 7.0 in the presence of different carbonate and calcium concentrations revealed that exposure to uranyl species in these conditions for short periods of time decreased cell viability, though cells grew at the same rate once they recovered. Cell viability decreased with increasing concentration of non-carbonato complexes of U(VI) in solution, suggesting that these complexes are bioavailable yet toxic at high concentrations. 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, and calcium conditions. Overall, these findings suggest that uranyl hydroxide complexes are the main bioavailable species to *Shewanella* and potentially explain why it does typically not grow efficiently on uranium at pH < 8. Incubations are currently conducted with *Geobacter bemidjiensis* isolated from Rifle to determine whether a similar effect is observed with other metal-reducing bacteria. In addition, well-mixed retentostat reactor experiments using sterilized native Rifle sediments inoculated with *G. bemidjiensis* are underway to study microbial reaction kinetics at low to near-zero growth rates and in conditions close to thermodynamic equilibrium.

NAME: Bradley Tebo
ORGANIZATION: Oregon Health & Science University
PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Manganese redox mediation of UO2 stability and U fate in the subsurface: Molecular and meter scale dynamics

ABSTRACT: Injection of electron donors into the subsurface to stimulate soluble U(VI) reduction to less soluble U(IV) species is being tested as an approach for in situ remediation of U contamination. The success of this approach depends on the long-term stability of U(IV). The reduction of Fe and Mn oxides during U(VI) reduction produces reduced metals which may later be oxidized forming strong oxidants such as MnO_2 after the addition of electron donor has ceased and oxidizing conditions return. The primary focus of our project has been on the interactions between Mn and U and with groundwater constituents and their effects on U(IV) stability.

The effect of Mn(II) on the UO_2 dissolution rate under reducing and oxidizing conditions was investigated. Under reducing conditions, a strong inhibitory effect was observed. Solid characterization suggested that precipitation of $MnCO_3$ may limit the exposure of U(IV) surface sites on UO_2 to trace level oxidants. In contrast, a promotional effect was observed under oxic conditions. It is hypothesized that Mn(II) adsorbed to UO_2 can be oxidized by dissolved O_2. The oxidation of Mn(II) could form reactive Mn(III) or Mn(IV) species, which could serve as additional oxidants for UO_2 that accelerate UO_2 dissolution. As an intermediate in Mn biogeochemical cycling, soluble Mn(III) has recently been found as an important environmental oxidant in oxic-anoxic interfaces. The kinetics of oxidative UO_2 dissolution by soluble Mn(III) stabilized by pyrophosphate was quantified. Soluble Mn(III) induced rapid UO_2 dissolution at a rate higher than by a comparable concentration of dissolved O_2. Self-consistent kinetic models were derived with excellent fits of the experimental results. The quantification of the reaction kinetics of oxidative UO_2 dissolution by soluble Mn(III) may help interpret the enhanced UO_2 oxidation mediated by Mn redox cycling and inferred from field measurements at Rifle, CO.

Our previous work in diffusion-limited agarose gels has shown that microbial Mn(II) oxidation did not enhance U(IV) oxidation by oxygen but that U(VI) produced was less mobile due to its sorption onto newly formed MnO_2. This past year we probed more complex sediment systems and evaluated whether the same outcome would be observed. Duplicate columns packed with Old Rifle sediments were run in the laboratory with an influent simulating Rifle groundwater, amended with U(VI) and either containing or devoid of sulfate. After U(VI) reduction and the accumulation of U(IV) over ~75 days, replicate columns were switched to an effluent containing 50 µM Mn(II) and 5% O_2 or only 5% O_2 to simulate oxidizing conditions. While microbial Mn(II) oxidation had been reported for unaltered sediments, the presence of U(IV) or the reducing conditions prevalent in the columns precluded significant Mn oxidation in the columns. However, the oxidation of U(IV) by O_2 was evident and led to the release of U(VI) in the effluent. We examined the microscopic distribution of U, Fe, S and Ca for columns before and after O_2 oxidation. In reduced sediments U was often associated with Ca but not directly with Fe or S. This suggests Ca adsorption to the surface of UO_2 as well as the association of Ca with non-crystalline U(IV). In the oxidized sediments, U was found primarily in association with S^0, iron sulfide minerals or $CaSO_4$, suggesting that the oxidation of S^{2-} by O_2 produces either S^0 or SO_4^{2-}. The implications of this work are that microbially mediated Mn(II) oxidation may be limited in reduced sediments despite the availability of O_2 and that the mechanism of redox buffering in sulfate-reducing sediments include the formation of S^0 and $CaSO_4$.

NAME: Ming Tien
ORGANIZATION: Penn State University
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Survival During Long Term Starvation: Global Proteomics Analysis of Geobacter sulfurreducens Under Prolong Electron Acceptor and Donor Limitation

ABSTRACT: Limitation/bioavailability of terminal electron acceptors (TEA) and electron donors is an environmentally relevant condition that affects the overall subsurface bioremediation process and efficiency. Microorganisms exist under "feast or famine mode" of survival, however they typically encounter famine conditions. *In situ* bioremediation technology uses indigenous microorganisms to treat large scale subsurface contamination. The technology relies on addition of suitable electron donors to subsurface sediments to stimulate bacterial activity. However, the high electron donor concentration conditions are artificial and transitory. Similarly TEA is also limited, we suggest that TEA-starvation conditions would evolve at injection wells after prolonged carbon addition. The work described here aims to understand the survival strategies of the anaerobe *Geobacter sulfurreduces* under both electron acceptor and electron donor limiting conditions.

Our results have demonstrated that *G. sulfurreducens* can survive under both TEA (fumarate) and electron donor (acetate) limiting conditions and displays five typical stages of growth: lag, log, stationary, death, and survival phases. The organism can sustain a stable population of ~10^6 cells/ml for over 2 years under TEA limiting conditions. Whereas it can sustain a higher population count of ~10^8 cells/ml for over 1 year under electron donor limiting conditions. Global comparative proteomic analysis was performed using iTRAQ and proteins varying in abundance with a high level of statistical significance ($p<0.05$) were identified. Under TEA starvation, 103 proteins were identified to be significantly up-regulated compared to 85 significantly down-regulated in survival phase cells as compared to mid-log cells. The most highly represented and significantly up-regulated proteins in the starved cells are involved in energy metabolism, cell envelope, and transport and binding functional categories. The majority of them were found to be localized in the cell membranes. The above results suggest that changes in the outer and cytoplasmic membrane are important in the survival of *Geobacter* under the aforesaid conditions. The cell shuts down anabolic processes and is poised, through changes in its membrane proteins, to sense nutrients in the environment, to transport nutrients into the cell and finally to detect/utilize TEAs it may encounter. Under TEA-limiting conditions, the cell is also highly reduced with minimal change in energy charge. Therefore, our proteomic and biochemical results indicates that even under TEA starvation, cells are well suited for bioremediation via reduction of radionuclides. The proteomic analysis of acetate starved cultures identified only 27 significantly up-regulated proteins compared to 196 significantly down-regulated in survival phase cells as compared to mid-log cells. Most of the up-regulated proteins belonged to energy metabolism, transport and binding, and protein fate functional categories. Most of the down-regulated proteins were ribosomal, transcription and translation proteins involved in protein synthesis, similar to TEA starvation condition. Here again, the majority of the up-regulated proteins were predicted to localized in the cytoplasmic membrane, and most of the down-regulated proteins were predicted to be localized in the cytoplasm. So far we were able to demonstrate that *Geobacter* can survive long-term nutrient limiting conditions and the differences in protein levels between the growing and starved cells. We will further investigate the genetic basis of the survival capacity by genomic sequencing.

NAME: Albert Valocchi
ORGANIZATION: University of Illinois at Urbana-Champaign
PROGRAM AFFILIATION: SBR

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

ABSTRACT: Bioremediation is being investigated as an effective strategy 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 H_2 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.

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. Selenite was chosen as a representative metal and was reduced to an insoluble precipitate inside the microfluidic reactor by *Anaeromyxobacter dehalogens*. Precipitates were analyzed by Raman spectroscopy and energy dispersive spectroscopy to confirm the presence of reduced selenium. The density of bacteria appeared greatest on the edges of the red precipitates, suggesting that microenvironments favorable for selenite reduction and growth occur near existing crystals.

Microfluidic experiments were modeled in 2-D to predict biomass distribution and chemical mixing at the pore scale in homogenous soils. Electron donor and acceptor were delivered through the inlets and mixed occurred along the centerline by transverse diffusion. Results indicate that microbes grow along the entire centerline where mixing occurs, that shear stress mitigates growth in pore throats but promotes growth in pore bodies, and that literature parameters for growth kinetics obtained from batch reactors can be used to simulate reactive transport at the pore scale.

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.

NAME: Scott Wankel
ORGANIZATION: Woods Hole Oceanographic Institution
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Multi-isotope tools for understanding interactions of nitrogen cycling with iron and uranium in the subsurface

ABSTRACT: As the most ubiquitous contaminant anion in groundwater sediments at US DOE sites, high levels of nitrate (NO_3^-) also co-occur with one or more priority contaminant metals or radionuclides. This project seeks to improve our understanding of subsurface biogeochemical nitrogen cycling and its multifaceted interactions with redox–active elements, in particular iron, in order to better predict the fate and transport of the widespread radionuclide uranium (U) in complex subsurface environments. In particular, bioremediation efforts focused on immobilizing U through stimulation of microbial reduction of U(VI) to U(IV) are inhibited by the presence of NO_3^-. Furthermore, the potential for introduction of nitrate-contaminated groundwater poses a direct and serious threat to the stability of uranium immobilization in subsurface sediments both directly, through the oxidation of U(IV) by NO_3^- and/or the reductive intermediate NO_2^-, or indirectly by coupling of N and Fe cycling. As such, the interpretation of the results of field–scale bioremediation studies are often complicated by the fact that several competing processes occur simultaneously. Through the use of new and integrated multi-isotope tools, which represent naturally occurring spatial and temporal integrators of cycling processes, this project aims to improve the detection of biogeochemical changes in the subsurface, particularly those involving the direct and/or indirect coupling of nitrogen cycling to U(IV) oxidation and mobilization. Specifically, the use of coupled isotope systems (e.g. $^{15}N/^{14}N$ and $^{18}O/^{16}O$ and the ratio of their respective isotopic fractionation or $^{18}\varepsilon:^{15}\varepsilon$) provides an even more powerful constraint on quantifying the relative roles of simultaneously occurring cycling processes in the context of subsurface redox transformations, including those responsible for U mobilization.

Experiments were conducted to characterize the N and O kinetic isotope effects of abiotic reduction of both NO_3^- and NO_2^- by Fe(II) as a starting point for characterizing linkages among subsurface N, Fe and U cycling at the field-scale. Results indicate substantial reduction of both NO_3^- and NO_2^- by Fe(II) in both the presence or absence of iron oxyhydroxides minerals. A range of N and O kinetic isotope effects (for both NO_3^- and NO_2^-) were observed across experimental conditions ($^{15}\varepsilon_{NO3}$ = 6.8 to 32.7‰, $^{18}\varepsilon_{NO3}$ = 3.4 to 19.7‰; $^{15}\varepsilon_{NO2}$ ~11.5‰, $^{18}\varepsilon_{NO2}$ ~4-6‰). Importantly, in all cases, abiotic reduction of either NO_3^- or NO_2^- by Fe(II) exhibited smaller O isotope effects than N isotope effects ($^{18}\varepsilon:^{15}\varepsilon = 0.4$ to 0.7). In contrast to canonical denitrification ($^{18}\varepsilon:^{15}\varepsilon = 1$), values of $^{18}\varepsilon:^{15}\varepsilon$ in NO_3-contaminated groundwaters commonly fall between 0.5 and 0.8. As such, our results point to a potentially widespread importance of Fe (II) based N reduction in these environments.

During the next phase of characterization, a series of 17 flow-through natural sediment columns was run for ~60 days under reducing conditions. In a subset of columns, Fe reduction was allowed to occur for 30 days, followed by the addition of NO_3^-. Multi-isotope data showed prominent shifts in $^{18}\varepsilon:^{15}\varepsilon$ over the course of NO_3^- addition and are interpreted as reflecting a shift from an initial Fe(II)-based reduction of NO_3^- to NH_4^+ to the onset of biological denitrification (NO_3^- reduction to N_2). Based on these results, we posit that tracking changes in NO_3^- and NO_2^- concentration and $\delta^{15}N$ and $\delta^{18}O$ along with aqueous and solid phase U and Fe chemistry in future experiments will allow partitioning of the specific N reducing processes directly and indirectly related to U(IV) reoxidation and mobilization under advective flow.

NAME: Karrie Weber

ORGANIZATION: University of Nebraska-Lincoln

PROGRAM AFFILIATION: SBR

ABSTRACT TITLE: Impact of viral infection of microbiota on subsurface biogeochemistry

ABSTRACT: Microbially mediated metabolisms have been identified as significant factors either directly or indirectly impacting biogeochemical cycling. To date the role that viruses play a significant role influencing microbial mortality and resulting community in terrestrial sedimentary systems is poorly understood. The objective of this project is to investigate viral infection of subsurface bacteria and the formation of contaminant-bearing viral particles and approached by examining the following hypotheses: (*i*) subsurface microorganisms are susceptible to viral infections, and (*ii*) viral surfaces will adsorb heavy metals and radionuclides.

In an effort to assess the significance of viral infection in subsurface microbial communities, the production of viral like particles in response to biostimulation was investigated by amending sediment slurries with dissolved organic carbon (^{13}C-labeled acetate) and nitrate. This stimulation resulted in the production of VLPs (Virus to Bacteria ratio ca. 480 to 2,400). Interestingly, the production of VLPs was positively correlated with acetate consumption and $^{13}CO_2$ production; whereas changes in bacterial abundance were correlated neither with acetate consumption or $^{13}CO_2$ production. Thus, indicating that viruses contribute to cell lysis and are sensitive indicators of microbial activity. Furthermore, the microbial community shifted from one favored by Betaproteobacteria to Gammaproteobacteria. This could simply be a result of "killing the winner" or microbial cell lysis could cross-feed the microbial community. These results suggest that viral infection could be playing a role in carbon flux thereby altering available carbon pools in subsurface environments.

The *in situ* addition of O_2 into a reduced well field at the Old Rifle Field site, well-field Exp. Plot C, resulted in an increase in VLPs in background and stimulated wells ($9.5 \times 10^5 – 3.1 \times 10^6$ in CU01; $2.2 \times 10^6 – 3.2 \times 10^6$ in CD01, respectively), suggesting viral response during redox shifts. VLP abundance decreased ($3.1 \times 10^6 – 1.3 \times 10^6$ in CU01; $3.2 \times 10^6 – 3.2 \times 10^5$ in CD01) concurrent with a sharp change in geochemical parameters of the aquifer 21-28 days after injection. The VLP abundance decrease was associated with an increase in the ORP, decrease in pH and Fe(II) concentration and increase in sulfide concentrations. Viral abundance fluctuated with geochemical changes; whereas cell abundance did not similarly respond. This result is consistent our prior laboratory experiments demonstrating a correlation between carbon consumption and viral abundance, but not cell abundance. Together these results indicate that virus-to-cell ratio and viral abundance may be better indicators of biological activity than cell abundance alone as dynamic viral infection mediates cell lysis.

The production of VLP's in groundwater has implications for nanoparticulate carbon or metal transport. Initial experiments indicate that metals (Zn^{2+}) will adsorb to the surface of *Escherichia coli* phage T4. Interestingly, as Zn^{2+} concentrations increased (ca.60 μM), infectivity increased. Results demonstrated an increase of plaque forming units (PFUs) for viruses incubated with Zn^{2+} relative to negative controls. Thus, indicating that Zn^{2+} enhances the infectivity of phage T4. Together, the results suggest that the sorption of metals to the surface of viruses could not only contribute to nanoparticulate transport but could also enhance infectivity further contributing to cell lysis. It is therefore necessary to establish potential relationship(s) between viruses, cells, carbon, and metals/radionuclides to provide sufficient scientific understanding to incorporate coupled physical, chemical, and biological processes into agent based and reactive transport models.

NAME: Ming Ye

ORGANIZATION: Florida State University

PROGRAM AFFILIATION: SBR

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

ABSTRACT: Subsurface environmental systems are open and complex, in which intricate biogeochemical processes interact across multiple spatial and temporal scales. Understanding and predicting system responses to natural forces and human activities is indispensable for environmental management and protection. However, 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. The proposed computational Bayesian framework is expected to be general and applicable to gain insights into subsurface biogeochemical processes that occur across a wide range of field sites and environmental conditions.

In the first year of the project, we are focused on attaining the first object to develop 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 is implemented using Bayesian network. In the network, model components (deterministic and stochastic) are separated into network nodes, and relations between the components are represented by network edges, which are also pathways of uncertainty propagation. To evaluate the developed method, a Bayesian network was developed for model scenarios of flooding and precipitation, groundwater flow and reactive transport problems. Contribution of different uncertainty sources to predictive uncertainty was quantified.

Uncertainty quantification within the network is conducted using the state-of-the-art sparse grid methods, which are computationally efficient and can be integrated with the Bayesian network seamlessly. The sparse grid methods can alleviate the problem of curse-of-the-dimensionality of conventional Monte Carlo methods by selecting a small number of sparse grid points (in parameter space) to evaluate statistical moments of quantities of interest. On the other hand, the sparse grid methods can also be used to develop a surrogate of the original model, a polynomial-like interpolation that is fast to evaluate. We have applied the sparse grid methods to groundwater flow and reactive transport problems. Since reactive transport problems are more challenging because of model nonlinearity, more advanced sparse grid methods are necessary such as high-order stochastic collocation method with adaptive schemes.

To thoroughly evaluate the developed methods, a synthetic problem of hexavalent uranium (U(VI)) reactive transport was developed based on data and information at the Naturita UMTRA site. The synthetic problem considers three geological settings, three kinds of boundary conditions, and nine geochemical reactions. We are conducing uncertainty quantification using conventional methods, and the results will be used to evaluate computational efficiency and accuracy of the sparse grid methods. The computational tool will be used to the real-world modeling at Naturita to gain insights into groundwater reactive transport modeling.

TERRESTRIAL ECOSYSTEM SCIENCE

ARGONNE NATIONAL LABORATORY (ANL)

NAME: Julie Jastrow
ORGANIZATION: Argonne National Laboratory
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Soil Carbon and Nitrogen Responses throughout Twelve Years of Atmospheric CO2 Enrichment in Deciduous Forest

ABSTRACT: The impact of atmospheric CO_2 enrichment on soil organic matter (SOM) dynamics and stocks depends on the interplay between plant responses, the soil's capability to protect and stabilize SOM against decomposition, and nutrient availability. Information on C and N allocation to functionally meaningful SOM pools and their dynamics can improve our understanding of soil responses and facilitate predictions of the potential for long-term stabilization. At the sweetgum free-air CO_2 enrichment (FACE) experiment in Oak Ridge, Tennessee, we used (1) repeated sampling over time, (2) the ^{13}C tracer provided by the fossil fuel source of fumigation CO_2, and (3) physical fractionation to determine the fate and dynamics of FACE-derived detritus inputs to SOM. Samples collected in years 0, 3, 5, 8, 10, and 12 of the experiment were fractionated to separate particulate organic matter (POM) and silt- and clay-associated organic matter protected by occlusion in stable microaggregates from their more readily dispersible counterparts. In this aggrading system, significant linear increases in bulk soil C and N occurred in the surface 5 cm of both ambient and elevated CO_2 treatments during the 12 years of the experiment, but accrual rates doubled in response to CO_2 enrichment – with no treatment effect on C:N ratio. "New" FACE-derived C accounted for the 12-year increase in bulk soil C and also replaced 30% of the "old" pretreatment C. Below the surface 5 cm, bulk soil C tended to increase to a depth of 45 cm, but these trends were not significant and did not differ between ambient and elevated CO_2 treatments. The difference in SOM accrual between elevated- and ambient-CO_2 treatments in the surface 5 cm occurred mostly in silt-sized and fine POM fractions. Initially, occlusion within microaggregates facilitated much of this accrual. But in years 8 and 10 during a prolonged drought, microaggregate-occluded C and N were transferred to non-aggregated pools. In year 12, after the drought ended, the quantities of silt-associated SOM occluded in microaggregates recovered to pre-drought levels. However, microaggregate-occluded POM continued to decline. This finding, coupled with an observed lagged/phased cycling of "old" pretreatment C through some SOM pools, suggests that continued SOM accrual might not be sustained for an extended time period – given that net primary production has declined at the site over time. The sensitivity of physical protection mechanisms to climate has implications for the potential long-term stability of accrued SOM in this system and those with similar soil characteristics. Beyond the CO_2 treatment responses, the isotopic tracer and observed dynamic changes contribute to understanding of SOM cycling and stabilization processes and provide data for model calibration and validation.

NAME: Julie Jastrow
ORGANIZATION: Argonne National Laboratory
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Climatic and edaphic controls over root decomposition and leaf litter inputs to components of mineral-associated soil organic matter

ABSTRACT: Soil organic matter (SOM) represents the largest reservoir of C in terrestrial ecosystems and climate change is expected to modify soil C dynamics. Further, the contributions of root- versus leaf-litter sources to 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 ^{14}C-enriched root- and leaf-litter manipulations at four sites representing the climatic extent of Eastern deciduous forest. These sites span a range of soil types and mean annual temperature and precipitation. We followed root decomposition and incorporation of root-derived C into soil. We also assessed inputs of leaf-derived C into acid-hydrolyzable and acid-resistant C pools of the mineral-associated dense fraction of site soils. Our results showed that the enriched root mass in root decomposition bags decreased over time, averaging 73% at T3 (1Y), 58% at T4, and 44% at T6 (3Y). Root decay constants were significantly affected by climate and edaphic factors. Soils in root incubation bags showed ^{14}C enrichment after only one month, suggesting that root C was quickly transferred to SOM, perhaps mostly as microbial residues. After the first month, soil ^{14}C enrichment exhibited cyclic dynamics that varied by site, which were likely related to site differences in microbial activity and edaphic factors affecting SOM stabilization. After 3 years, the average root-derived C retained in the soil varied depending on site but, on average, accounted for 3% of total root decomposition inputs. The two sites with the highest soil C concentrations were also the sites that retained the most root-derived C, at about 5% of the total inputs. Across the EBIS sites, about 60% of the C in the soil dense fraction was acid-hydrolyzable, and C turnover in this fraction was 1-2 orders of magnitude faster (~35-350 y) than that of the acid-resistant fraction (~300-1500 y). Two years after the addition of ^{14}C-enriched leaf litter, no detectable leaf-derived C signal was seen in either fraction at the two sites with the highest soil C concentrations. At the warmest and wettest site, where turnover times were generally the fastest, leaf-derived ^{14}C was detected in the acid-hydrolyzable fraction at depths of both 0-5 and 5-15 cm. The acid-resistant fraction was also enriched with leaf-derived ^{14}C at 0-5 cm, possibly as a result of bioturbation by earthworms. At the site with the lowest soil C, leaf-derived ^{14}C was found in the acid-resistant fraction near the soil surface (0-5 cm). But, the lack of leaf-derived ^{14}C in the acid-hydrolyzable fraction suggests this potentially bioactive pool is not well protected by the sandy soils at this site. Overall, we found climatic and edaphic effects on root decomposition and mineral-associated SOM dynamics, which can contribute to model calibration and validation.

NAME: Roser Matamala
ORGANIZATION: Argonne National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Biological invasions impact ecosystem properties and can affect local climate predictions

ABSTRACT: We studied the impacts of vegetation and weather variations on carbon and energy fluxes at a restored tallgrass prairie in Illinois. The prairie was a strong carbon sink, despite a prolonged drought period and vegetation changes due to the presence of a non-native biennial plant. Albedo and energy fluxes were similarly affected by drought and vegetation changes. Drought reduced latent heat and sensible heat fluxes because of the lack of precipitation and depleted soil water content, which decreased the water available for evapotranspiration. In addition, lower plant productivity and reduced plant canopy density increase radiation reaching the surface soil. The reduced LE and increased H resulted in a higher Bowen ratio (H/LE) by 51%, than in normal-precipitation years. Although the growing season of 2006 experienced normal precipitation, soil water content, and soil temperature, the dominance of the non-native *M. alba* resulted in a Bowen ratio similar to that under the drought conditions as a consequence of reduced LE and increased H fluxes. These effects on energy fluxes are most likely due to differences in the canopy structure and phenology of *M. alba* versus native vegetation. *Melilotus alba* forms very dense canopies that (1) effectively reduces incoming radiation to the soil surface, thus reducing the energy available for evaporation, and/or (2) physically reduces the exchange of heat with the atmosphere. Furthermore, vegetation changes reduced the C uptake period in 2006 by disrupting the typical seasonal succession of C_3 and C_4 prairie plants and reducing the transpiration flux and enhancing H flux, particularly after *M. alba* senescence in early August. Reduction in daily mean albedo supports the hypothesis that plant phenological changes, not climate, affected energy fluxes during that year. Vegetation changes had the strongest effect on C cycling, reducing net ecosystem production by 55%, compared to a 50-year drought year and by 68% compared to normal precipitation years. We use a modeling approach to separate the effects of environmental drivers and biotic responses on net ecosystem exchange. Analysis of the model predictions suggest that the vegetation factor was more important than abiotic factors in describing changes in C fluxes at this grassland site. Changes in species dominance had the strongest effect in reducing net ecosystem production and albedo and increasing sensible heat flux. These effects may result in positive feedbacks on warming and microclimate changes.

TERRESTRIAL ECOSYSTEM SCIENCE

LOS ALAMOS NATIONAL LABORATORY (LANL)

NAME: Nate McDowell
ORGANIZATION: Los Alamos National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Testing the effects of heat and drought on plant mortality and survival

ABSTRACT: Drought-related, continental-scale forest mortality events have been observed with increasing frequency during the past 20 years. These events have affected tropical rainforests, temperate mountainous and Mediterranean forests, and boreal forests. 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. Thus, regardless of future predicted precipitation, periods of low rainfall may cause greater mortality due to higher temperature.

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. 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. 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 controlling the climate in open top chambers. The temperature in the chambers is kept at 5°C above ambient all the time. In this presentation we show results from the first year of the experiment. No trees have died yet, but the treatments work as expected, and after a very dry winter, tree mortality is anticipated this coming summer.

TERRESTRIAL ECOSYSTEM SCIENCE

LAWRENCE BERKELEY NATIONAL LABORATORY (LBNL)

NAME: Jeffrey Chambers
ORGANIZATION: LBNL
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Toward a Predictive Understanding of BVOC Emissions from Tropical Forests

ABSTRACT: Emission of biogenic volatile organic compounds (BVOCs) from the Amazon Basin impacts key atmospheric processes including aerosol and cloud lifecycles, which in turn influences terrestrial physiological processes through changes in precipitation, temperature, and the quality of incoming light for photosynthesis. Our ability to represent these coupled biosphere-atmosphere processes in Earth system models (ESMs) is constrained by an extremely poor understanding of the identities, quantities, and seasonal patterns of BVOC emissions from tropical forests and a mechanistic understanding of their plant physiological and environmental controls. To fill these knowledge gaps and improve predictive ESMs, the Green Ocean Amazon Terrestrial Ecosystem project (Geco) is designed to evaluate the strengths and weaknesses of leaf and ecosystem-scale BVOC emission algorithms for forests near Manaus, Brazil. We first evaluated BVOC emission algorithms by measuring leaf BVOC emissions and assimilated carbon responses of a tropical species (mango, *Mangifera indica*) in a controlled, laboratory experiment. We applied a novel $^{13}CO_2$ labeling technique to observe, for the first time, the dynamics of stored versus recently assimilated carbon sources for BVOC emissions and its dependencies on light and temperature. The results suggest an important functional role of isoprene under high temperature stress where stored carbon sources increasingly dominate diminishing photosynthetic sources to sustain high isoprene emissions. Evaluation of the Community Land Model (CLM), which includes the Model of Emissions of Gases and Aerosols from Nature (MEGAN), over the Central Amazon region, showed a stronger response of isoprene emissions to varying temperature than light. Additional sensitivity tests with MEGAN-CLM (internal CO_2, soil moisture, plant functional type) will be used to develop a detailed Geco field study near Manaus, Brazil. This BVOC field study, will in turn, be used to recommend parameter and structural changes to MEGAN-CLM.

The Geco field study will;

1) Take advantage of extensive historical forestry datasets together with unique canopy access in the ZF2 forest preserve Amazon field site with walkup flux towers, a canopy access lift, and canopy walkways**.** Using environmentally controlled leaf chambers, we will study large numbers of tree species for **relationships** between environmental variables (light and temperature) and plant physiological variables (photosynthesis, transpiration, conductance, and emissions of BVOCs)**.**
2) Apply positional specific ^{13}C-labeled metabolite feeding to track intra and extra cellular carbon sources into BVOC biosynthesis and emission. BVOC carbon source(s) dependencies on envirionmental variables (light, temperature) will be evaluated using novel positional-specific ^{13}C-metabolite labeling techniques with a variety of BVOC precursur substrates including $^{13}CO_2$, $H^{13}CO_3^-$, ^{13}C-pyruvate, ^{13}C-ethanol, ^{13}C-acetate, and ^{13}C-glucose.
3) Estimate within and above canopy BVOC fluxes from high vertically resolved ambient concentration measurements in primary rainforest canopy in the central Amazon in relation to environmental drivers (light, temperature, soil moisture) in order to elucidate the role of BVOC biosynthesis and emission processes in response to seasonal climate variables.

NAME: Marc Fischer
ORGANIZATION: LBNL
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Full-column Greenhouse Gas Profiles Measured at ARM SGP

ABSTRACT: The vertical distributions of CO2, CH_4, and other gases provide important constraints for the determination of terrestrial and ocean sources and sinks of carbon and other biogeochemical processes in the Earth system. Remote sensing from ground-based and satellite-borne platforms require in-situ validation. We report results from a collaborative measurement campaign between the DOE Biological and Environmental Research Program (DOE-BER) and the NOAA Earth System Research Laboratory (NOAA-ESRL) to quantify the vertically resolved distribution of atmospheric carbon-cycle gases (CO_2, CH_4, 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, we conducted 6 successful 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. In the coming year we plan to compare Aircore measurements with NASA remote sensing, and begin a transition from research-mode to operational balloon-borne sampling that includes semi-automated recovery and on-site gas analysis at ARM-SGP. The expected outcome of this project will be an operational capability providing data that supports key DOE science objectives.

NAME: Caitlin Hicks Pries
ORGANIZATION: Lawrence Berkeley National Laboratory
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: The vulnerability of subsurface soil organic carbon to in situ warming and altered root carbon inputs: a project of the LBNL TES SFA

ABSTRACT: Subsurface soils (>30 cm) store more than half of global soil organic carbon (SOC) and the processes governing soil C turnover vary with depth. However, most SOC research has focused on surface soil; thus controls on subsoil dynamics are poorly understood. We are developing a whole soil profile (to 1.5 m) warming experiment in an annual grassland to study the effects of warming and root inputs on SOC dynamics throughout the profile. In the prototype, we will insert resistance heaters to heat the soil profile to 4°C above ambient while maintaining its natural temperature gradient. Highly ^{13}C-enriched *Avena fatua* grass root litter will be added to three depths within heated and unheated plots. A comprehensive suite of measurements—instrumented *in situ* and in the laboratory—will be used to quantify the effect of warming and carbon inputs on soil C cycling. To improve predictive understanding and model skill, the experiment is focused on hypotheses concerning: (1) temperature sensitivity of native SOC and added root litter (or DOC) decomposition with depth; (2) the priming effects of added root litter (or DOC) on native SOC decomposition with depth; and (3) interactions between warming and added root inputs. This study is one of the first to study responses of subsurface SOC to global change factors *in situ* and is designed to enhance our understanding of deep SOC stabilization mechanisms and improve predictions of SOC's fate in a changing climate.

As a central part of the LBNL Terrestrial Ecosystem Science Scientific Focus Area, this experiment is being developed in concert with vertically resolved soil organic matter models (see Riley and Tang posters) to be integrated into CLM. The experiment is designed to produce new process level understanding and data to test and develop new model structures, parameters, and projections.

NAME: Jennifer Holm
ORGANIZATION: Lawrence Berkeley National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Disturbance-Recovery and Climate System Feedbacks from Tropical Forests

ABSTRACT: Large uncertainties remain surrounding vegetation and carbon responses in the Amazon forest to disturbance parameters including size, rates, spatial distribution, and return frequency. It has been long recognized that forest sample plots are embedded in larger landscapes consisting of varying disturbance regimes. Here, we studied the impacts of prolonged increased disturbance on a tropical forest and evaluated the steady-state mosaic of disturbance and succession across an old-growth Central Amazon forest. To help quantify the impacts of increased disturbances on the climate system, the accuracy of tree mortality in global land surface models (here the Community Land Model, CLM) warrants improvement. To address this issue, we parameterized, calibrated, and verified ZELIG-TROP, a dynamic vegetation gap model, to simulate a complex Central Amazon forest and improve disturbance-recovery processes in CLM. Under a high disturbance scenario (doubling background tree mortality annually) the dynamic vegetation model predicted that aboveground biomass and net primary productivity decreased by 41.9% and 8.4%, respectively, and turnover rates increased by 42.3%. In addition, there were a higher proportion of smaller stems (20.7%), and a decrease in larger stems, producing a decrease in annual coarse litter inputs (trunks and large branches >10 cm in diameter) by 7.1%. This reduction in coarse litter resulted in a carbon flux gain, which over the long term (>100 years) offset the total loss in standing live biomass. The largest discrepancies were that under a high disturbance, CLM did not capture the temporal variability in carbon flux with respect to disturbance, nor did CLM replicate the reduction in coarse litter over the long-term and gains in carbon flux. By integrating field plot data, remote sensing disturbance probability functions, and modeling approaches, results demonstrate that a steady state of patches of varying successional age occurs over a relatively large spatial scale. Additionally, as found here using a model-based analysis of fractional mortality across all gap sizes demonstrated that 9.1–16.9% of tree mortality was missing from plot-based approaches, underscoring the need to combine plot and remote-sensing methods for estimating net landscape carbon balance. This study highlighted important implications for detecting temporal trends on plots that sample a small fraction of the landscape. To maximize the detection of global change temporal trends for this Central Amazon site (e.g., driven by CO2 fertilization) plots larger than 10 ha would provide the greatest sensitivity. Lastly, in order to predict a more dynamic and accurately responsive carbon signal to disturbances in global climate modeling, the mechanistic and stochastic mortality algorithms used in ZELIG-TROP should replace the procedure used in CLM.

NAME: Janet Jansson
ORGANIZATION: LBNL
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Impact of fire and natural thaw on permafrost microbial communities and functions

ABSTRACT: Permafrost currently sequesters a large fraction of the terrestrial carbon that is susceptible to microbial enzymatic processes as the permafrost thaws. We aimed to determine the impact of natural thaw as well as increased soil temperatures due to fire on permafrost microbes and functions using a variety of omics approaches. The sampling sites were in central Alaska: 1. Nome Creek, the site of the Boundary fire in 2004; and 2. Tanana Valley, a boreal forest region where natural thaw has resulted in thermokarst bog formation. Replicated samples were taken from surface, active layer samples, as well as from permafrost in the different depths and DNA was extracted and sequenced. In addition, RNA and proteins were extracted from the Tanana Valley samples to provide information of gene expression and activity. We found that both natural thaw and fire had a dramatic impact on the composition and function of the permafrost microbial communities. The results indicated that there were specific microbes that were more abundant in permafrost compared to thawed soil at the same depth. The types of functions that were detected in permafrost included those for nitrogen assimilation and stress tolerance. The microbial activity was much lower in the permafrost compared to thawed samples, based on the lower gene expression in permafrost. By contrast, there were many shared functional genes that were expressed in seasonally thawed active layer and bog samples, including transporters. After thaw there was an increase in genes and proteins for methanogenesis in the bog, but due to the decrease in carbon content after fire this was not the case at Nome Creek. These findings suggest that rapid thaw due to fire has different consequences on carbon cycling processes compared to more gradual thaw, something that should be taken into account in future climate models.

NAME: Jinyun Tang
ORGANIZATION: Lawrence Berkeley National Laboratory
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: A microbial organic matter decomposition model based on the dynamic energy budget theory and trait-based modeling approach: model structure and preliminary analysis

ABSTRACT: Organic matter decomposition involves the close coupling between abiotic soil processes and biotic microbial processes. We contend that, to inform land-atmosphere greenhouse gas fluxes in an earth system model, a biogeochemical module should consistently represent the interactions between microbial community structure, microbial activity, and soil biogeochemistry. Here, we propose a model structure that integrates the dynamic energy budget (DEB) theory and a trait-based modeling (TBM) approach to characterize soil microbial processes relevant to carbon and nutrient cycling. The DEB enables an explicit representation of the intracellular metabolic reserves and structural pools, while the TBM explicitly describes the distribution of microbial guilds and functional pathways across spatial and temporal environmental gradients. This formulation allows us to dynamically model changes in microbial stoichiometry in response to changes in substrate diversity and availability. We have integrated this DEB-TBM framework with an equilibrium chemistry approximation approach. The coupled model framework allows for a generic model structure that can consistently simulate microbial functional diversity and fitness under the influence of abiotic mineral adsorptive surfaces and other subsurface protection mechanisms.

We applied this model structure to simulate aerobic organic matter decomposition by a few different microbial functional guilds. By explicitly representing the extracellular-enzyme regulated cascade between different organic polymers and organic monomers, we formed an organic matter decomposition model that can model the close feedback between organic matter chemical composition and microbial ecology. Preliminary analysis indicates (i) the model reasonably simulates the often-observed two-phase behavior of litter decomposition and (ii) the chemical composition of the long-term decomposed organic matter becomes a function of both the initial organic matter chemical composition and the associated microbial community structure. We also discuss issues associated with integration of the approach in larger-scale biogeochemistry models.

NAME: Margaret Torn
ORGANIZATION: Lawrence Berkeley National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: LBNL Terrestrial Ecosystem Science SFA: Controls on Belowground Carbon Cycling

ABSTRACT: We conduct basic research with a focus on soil carbon cycling and its role in terrestrial biogeochemistry and climate feedbacks. We are addressing gaps in process-level understanding and data to improve ecosystem models of ecosystem-climate feedbacks and sequestration. Using a combination of field and laboratory experiments, natural abundance ^{14}C and isotopically labeled substrates, advanced imaging, and microbial ecology, we are currently studying:

- ##### Decomposition and stabilization of aboveground and belowground plant inputs. (1) Blodgett Forest. In 2001, we placed $^{13}C/^{15}N$-labeled roots and needles in Sierra Nevada soils. We are using the final 10-year collection to investigate the influence of litter type, soil depth, and microbial community on decomposition rates, pathways, and compound-specific stabilization. (2) EBIS-AmeriFlux. We are assessing soil density fractionations and quantifying ^{14}C-based turnover times of soil organic matter and ^{14}C-labelled leaves and roots at four AmeriFlux sites, as part of the multi-Lab Enriched Biosphere Isotope Study.
- ##### Physical and microbial processes of black carbon degradation.
- ##### Mechanisms of long-term soil organic matter stabilization. We are working to bridge from molecular mechanisms of carbon stabilization to multi-scale biogeochemical models, integrating experimental data and numerical simulation methods to improve terrestrial models based on new understandings of organic matter dynamics.

Example of a current project on: The effect of soil warming and soil depth on microbial decomposition of biochar, wood, and bulk soil organic carbon in contrasting temperate and tropical soils. We conducted an incubation study using soils from a moist tropical forest in Puerto Rico (PR) and a Mediterranean grassland in California (CA), collected from surface and deep horizons. We added ground ^{13}C-labeled biochar (or the wood from which it was derived) to these soils and incubated them at ambient and ambient +6°C temperatures (at field gravimetric moisture) for one year. There were distinct microbial communities in the four soil types according to 16SrRNA gene analysis. Wood decomposed approximately 35 times faster than did char, based on $^{13}CO_2$ evolution from the soils. Amendments in the surface decomposed faster than those in deeper soil at ambient temperature, and in forest faster than in grassland soil. Both substrates had $Q_{10}<2$, which was less than the temperature response of native SOC. Wood increased decomposition losses of the native soil organic carbon by ~30% in the grassland and slightly less in forest soil. Biochar had only a slight priming effect but stimulated Actinobacteria in the grassland soil, and α-Proteobacteria, Actinobacteria, and Acidobacteria in the tropical soil. Biochar addition was associated with a decline in cellulose and hemicellulose degrading enzyme activity in grassland soils. Based on ^{13}C analysis of soil density fractions, more biochar than wood was found physically protected fractions, and in the clay-rich deeper Tabonuco soil. Together, these results show that decomposition of these slow-cycling organic inputs is not sensitive to warming but is influenced by soil characteristics that vary with location and soil depth, independent of the type of material being decomposed.

NAME: Margaret Torn
ORGANIZATION: Lawrence Berkeley National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: The AmeriFlux Management Program: Overview

ABSTRACT: AmeriFlux is one of the DOE Office of Biological and Environmental Research's (BER) best known and most highly regarded brands in climate and ecological research. AmeriFlux datasets, and the understanding derived from them, provide crucial linkages between terrestrial ecosystem processes and climate-relevant responses at landscape, regional, and continental scales. The LBNL-led AmeriFlux Management Program (AMP) is working to enhance this important BER program. Our primary objectives are (1) maximize the quality of AmeriFlux data and its usability for a broad community; (2) expand the network's impact as a virtual facility for basic research and Earth System Model (ESM) improvement; (3) foster innovative measurements; and (4) sustain the long-term record of carbon, water, and energy fluxes and site metadata being collected by a cohort of AmeriFlux sites that span a spectrum of climate and ecological spaces across the Americas. We are working to (1) provide enhanced technical support, including quality assurance/quality control (QA/QC) and new data submission methods for the entire AmeriFlux network; (2) host an AmeriFlux Network website, organize the Annual Meeting, and conduct other outreach and community functions; (3) Support the operation of about 15 existing long-term AmeriFlux Core Sites; (4) produce standardized gap-filled datasets and tools that will enable modeling, synthesis, and other research with AmeriFlux data; (5) provide high-quality data and metadata to the Carbon Dioxide Information Analysis Center (CDIAC).

The Data Processing and QA/QC component of the Program will support all sites in the Network including the AMP-funded Core Sites. This component of the program will provide a centralized portal for data processing and management including: standardized data processing; data uncertainty estimation and quality flags; gap-filled, quality-assured, versioned data sets in conjunction with CDIAC; and advanced data reporting tools to aid data providers. We will archive and version high frequency data; and make data processing capabilities available to all AmeriFlux sites via our new, fast-evolving web portal.

Information on the AMP **Technical Support and QA/QC**, and the **Longterm Core Sites** of the AmeriFlux Network will be presented in this poster or an adjoining one.

Community Outreach and Engagement is being facilitated via our new website, the annual AmeriFlux meeting (next in 2014), and workshops. **The AmeriFlux Science Steering Committee (SSC)** is being maintained as an independent advisory group and augmented with a Science Advisory Board linking AmeriFlux to major stakeholders.

NAME: Margaret Torn
ORGANIZATION: Lawrence Berkeley National Laboratory
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: The AmeriFlux Management Program: Technical QA/QC for all AmeriFlux sites, and establishment of long term AmeriFlux Core Sites

ABSTRACT: The AmeriFlux Management Program (AMP) is enhancing the utility of AmeriFlux data on terrestrial fluxes of CO_2, water, and energy with increased technical support as well as by ensuring there are long term observational records. The AMP **QA/QC and Technical Site Support team** is strengthening the AmeriFlux network by standardizing operational, calibration, and maintenance activities, setting clear data quality goals, and helping to resolve discrepancies promptly. We are conducting site inter-comparisons with roving eddy covariance measurement 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 eight months the new AmeriFlux QA/QC lab at LBNL has transitioned from the prior AmeriFlux QA/QC lab at Oregon State University. The team is experienced in testing new instruments and working with manufacturers, and is building working relationships with both vendors and investigators. There are eight sites scheduled for QA/QC visits this first year. They have just completed their first site visit, where calibrations, QA/QC routines and tests were conducted, and

One of the most exciting opportunities in this project is **the stewardship of AmeriFlux Core Sites** as sources of comprehensive, high quality data for a broad range of research applications. We have identified a first set of ten exceptional AmeriFlux sites, most comprising a cluster of multiple towers, which will be funded and supported to form a backbone of long-term AmeriFlux research. These sites cover a range of ecosystem types and climate regions, complement other networks and sites, comprise coherent clusters of demography and disturbance, and are good choices for addressing important ecological questions. Our strategy is to support the PIs, who understand the observational challenges and research opportunities at their sites, while drawing them to a common standard for critical instruments and protocols. We are developing tools to assist them in data QA/QC and management, tracking instrument and calibration activity, data revisions, and recalibration effects on data. The Core Sites will generally have a full-time technician at each site-cluster to carry out or oversee instrument installation, routine maintenance, calibration, and QA/QC; initial data processing, ancillary data collection and sample processing; and PI-preferred processed data.

TERRESTRIAL ECOSYSTEM SCIENCE

LAWRENCE LIVERMORE NATIONAL LABORATORY (LLNL)

NAME: Karis McFarlane

ORGANIZATION: Lawrence Livermore National Laboratory

PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Elucidating the fate, transport and processes controlling carbon on the landscape: Biogeochemistry tools for the 21st century

ABSTRACT: A critical scientific question is what are the present day sources and sinks of carbon dioxide (CO_2) in the natural environment and how will these sinks evolve under rising CO_2 concentrations, expected climate change, ecosystem response, and land-use change. Globally, more carbon is stored in belowground as soil organic matter than in terrestrial vegetation and the atmosphere combined. This vast pool of carbon is derived primarily from decomposed plant and microbial cell material, and the fluxes that control the size of this pool are critical to the global carbon cycle. Carbon initially enters the belowground soil pools as plant detritus, roots and (root) exudates. Once in the soil, this organic matter serves as a carbon source for decomposer organisms including soil animals, bacteria, and fungi. Most of this carbon is consumed and respired as CO_2, but some is converted to microbial biomass and byproducts, which may leave the soil as dissolved organic carbon, be used as a substrate by other microbes, or be stabilized within the soil mineral matrix. Mechanisms that result in the stabilization of soils include: climate stabilization; intrinsic recalcitrance due to chemical structure; physical stabilization whereby organic molecules are in association with aggregates and mineral surfaces; and microbial metabolic activity and or protection of potential substrate due to physiochemical barriers. It is these processes that span time and spatial scales, which are poorly constrained in many dynamic land surface models.

We have deployed a suite of analytical tools that allow us to follow the movement of carbon at the cell to landscape scale. Experiments, field-based and *in vivo*, allow us to further the mechanistic understanding of the factors that control the fate, transport, and sequestration potential of, primarily, belowground carbon. Novel techniques include ChipSIP and STXM-SIMS. ChipSIP allows us, for example, to understand which microbial enzymes efficiently degrade cellulose - either for the production of biofuels, or to better elucidate enzymes and energy (carbon) transfer in wetlands and soils. To disentangle the complex interactions at soil-microbial-film-mineral interfaces with minimal disruption we utilize a combination of high-resolution spectroscopy (STXM-NEXAFS), electron microscopy, and nano-scale imaging mass spectrometry collectively known as STXM-SIMS. This approach allows us to measure the role of microorganisms in the formation of microaggregates and elucidate how organic matter source and environmental conditions influences the microaggregates. Isotopic characterization (^{14}C, ^{13}C, ^{2}H) of CH_4, CO_2, and physical sources of carbon provides the mechanistic fingerprints of the biogeochemical pathways that cycle carbon through the landscape. Building on our expertise for "conventional" graphite-based AMS-^{14}C analyses and our bio-expertise in tracer level pulse chase experiments we are developing methods for 'direct injection' of CO_2 for AMS-^{14}C analyses. Our initial focus has been on a liquid-sample (HPLC) sample interface. The ability to handle liquid samples and continuous flows of liquid will enable more widespread and routine use of AMS in biological and environmental applications.

NAME: Jessica Osuna
ORGANIZATION: Lawrence Livermore National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: A New Method for Reducing Uncertainty in Biospheric CO_2 flux: A case study at Tonzi AmeriFlux Site

ABSTRACT: While gaps in trace-gas fluxes measured via eddy-covariance occur for a variety of reasons, many occur at night due to a stratified (stable) atmosphere close to the surface. Currently, the community standard for eliminating data during periods of stability is to apply a threshold of friction velocity (u_*). Despite applying the u_* threshold, data often indicate net CO_2 uptake at night, casting doubt on whether a u_* threshold is accurately eliminating data from stable periods. Because most flux sites are only equipped with one set of instruments (usually just above the canopy), vertical profiles of turbulent transfer within and above the canopy are generally not available providing few alternatives to the u_* correction method within the FLUXNET community. The ability to better quantify atmospheric stability within and above the canopy would improve data quality assessment.

Here we present progress in applying the Advanced Canopy-Atmosphere-Soil Algorithm (ACASA) model to simulate turbulent exchanges of CO_2 and H_2O at the Tonzi oak savanna AmeriFlux site (Ione, CA). We also present vertical profiles of turbulence and wind shear measured within and above the canopy with an upward facing atmospheric LIDAR system. We validate ACASA flux outputs against eddy-covariance data and ACASA-generated profiles of wind shear and turbulence kinetic energy (TKE) against data from the LIDAR deployed at the site during multiple campaigns. We show the effect of assessing within- and above-canopy turbulent transfer (and thus vertical flux quality) via thresholds based on u_* (from eddy-covariance) versus vertical profiles of TKE (from ACASA and LIDAR). We especially focus on achieving an atmospheric understanding of why the commonly used u_* method for flux quality assessment diverges from results based on TKE.

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TERRESTRIAL ECOSYSTEM SCIENCE

OAK RIDGE NATIONAL LABORATORY (ORNL)

ORNL NEXT-GENERATION ECOSYSTEM EXPERIMENTS (NGEE ARCTIC)

ORNL SCIENTIFIC FOCUS AREAS (SFA)

NAME: Gautam Bisht
ORGANIZATION: Lawrence Berkeley National Laboratory
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Development of a Sub-meter Resolution Modeling Framework for Arctic Ecosystems: Coupling CLM and PFLOTRAN and Spatial Scaling Results

ABSTRACT: Arctic and sub-Arctic soils currently contain approximately 1700 billion metric tones of frozen organic carbon, approximately 200 times current annual anthropogenic emissions. This carbon is vulnerable to release to the atmosphere as CO_2 and CH_4 as high-latitude temperatures warm. The NGEE-Arctic project is working to optimally inform process representations in a global-scale model (CLM) with knowledge and understanding gained through direct observation and simulations using a process-resolving model (PFLOTRAN) at sub-meter scales. Polygonal ground, with a characteristic DEM length scale of ~15 m, is a common landscape type that occurs over large parts of Arctic tundra. These ground structures, with high or low centers, dominate the local hydrologic environment, thereby impacting the energy balance, biogeochemical dynamics, vegetation communities, and carbon releases from the subsurface.

In this poster, we first present spatial scaling results of soil moisture in the presence of polygonal features using coupled surface-subsurface flow PFLOTRAN simulations at multiple scales for the study site located near Barrow, AK. We describe the statistical moments of soil moisture fields across spatial resolutions, fractal scaling parameters, and a method to propagate spatial variability based on predicted higher-order moment relationships. Second, we present progress on integrating carbon and nitrogen biogeochemical (BGC) dynamics by implementing a CENTURY-like reaction network in this modeling framework, and the resulting impacts on BGC spatial scaling. Preliminary results demonstrate impacts of abiotic controls (e.g., surface interactions and temperature) on the long-term stabilization of soil organic matter in permafrost conditions. Third, we present preliminary results from the hydrologically coupled CLM-PFLOTRAN model that shows impacts of soil moisture redistribution on the simulated surface energy balance. Finally, we present a framework to extend CLM-PFLOTRAN modeling framework to include subsurface thermal coupling.

NAME: Baptiste Dafflon
ORGANIZATION: NGEE
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Advanced Characterization of Active Layer and Permafrost Variability using Geophysical Approaches

ABSTRACT: The arctic tundra ecosystem is recognized as a large source of uncertainty in quantifying feedbacks to global climate warming. Improving understanding of arctic ecosystem functioning and parameterizing process-rich models that simulate feedbacks to a changing climate require advances in estimating the spatial and temporal variations in active layer, ice-wedge and permafrost soil properties. In the context of the Next-Generation Ecosystem Experiments (NGEE-Arctic), we worked on the development of advanced geophysical strategies to improve arctic subsurface imaging and monitoring, as well as understanding interactions between soil properties and arctic ecosystem processes and dynamics. Some specific objectives involved improving (i) geophysical capability in characterizing different subsurface features, including active layer, ice-wedges, ground-ice, saline layers, and permafrost with variable ice-content, (ii) quantifying relations between soil-geochemical properties, geophysical, and geomorphological properties, (iii) integration of multi-scale and -resolution geophysical and point measurements, (iv) strategies to monitor freeze-thaw and water dynamics, and (v) estimates of properties (such as thaw depth, soil moisture, snow depth and water equivalent, ice content and geochemical parameters) and their uncertainty over scales that are relevant for modeling. These objectives were pursued through various numerical developments, laboratory experiments, and field investigations. Field investigations have been performed at the NGEE site located in the Barrow Environmental Observatory (BEO) near the coastal village of Barrow (AK), which is dominated by different types of ice wedge polygons. Acquired geophysical measurements include complex resistivity or electrical resistivity tomography (ERT), electromagnetic induction (EMI) data using portable tools, multichannel analysis of surface waves (MASW) seismic data, ground-penetrating-radar (GPR) data, and time-domain reflectometer (TDR) data. Petrophysical, geochemical, snow point measurements, as well as airborne LiDAR data were used to constrain the interpretation of the geophysical data.

Our major recent advances include (i) a novel parameter-estimation approach adapted to explore the solution non-uniqueness inherent to EMI data and importantly to estimate quickly both electrical conductivity variations in the active layer and trends in permafrost distribution over large areas as enabled by the extensive spatial coverage of EMI data, (ii) an unconventional full-waveform method for MASW data that is especially suitable for resolving low seismic-velocity features that may be associated with permafrost soils with abundant unfrozen water, (iii) high-resolution imaging of ice-wedges, permafrost and active layer using multi 2D ERT at a high-spatial resolution that enables identification of properties that vary substantially over length scales of less than a few meters, (iv) understanding the complex resistivity electrical signature of the freeze thaw states and transitions of arctic soils trough column experiments that will serve for setting field monitoring, (v) an advanced hierarchical Bayesian model for integrating multiscale, multi-type point/geophysical/remote-sensing datasets that provide estimates of subsurface properties and their associated uncertainty, and (vi) identification of relations between subsurface properties and surface properties that can serve for zonation at larger scales and/or parameterization of mechanistic models. The above developments will facilitate the identification and modeling of critical terrestrial ecosystem characteristics and behaviors.

NAME: Ranjeet Devarakonda
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: TES»

ABSTRACT TITLE: NGEE Arctic Data Management – Status and Planned Activities for 2013

ABSTRACT: The open sharing of data and information among the NGEE team, the broader scientific community, and the public is critical to meeting the scientific goals of the Next Generation Ecosystem Experiment (NGEE) Arctic project.

In implementing the integrated approach, the project is generating diverse data sets from observations, experiments, and models across field plot, polygonal landform, regional, and global scales and is drawing in a wealth of existing data products collected and generated by other research organizations across the Arctic.

Developing the data management infrastructure to support this approach is a significant challenge. Nonetheless, the NGEE Arctic project is committed to upholding rigorous and high-quality data management strategy and the implementation of that strategy in an innovative, cost-effective data collection, management, distribution, and archival framework.

The NGEE Arctic Data portal will support the current research in Barrow and provide a consistent framework to support future research efforts as they expand to other regions.

This poster illustrates the 2013 NGEE Arctic Data Management Activities.

NAME: David Graham
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Biogeochemical controls on microbial CO2 and CH4 production in anoxic low-centered polygon soils from the Barrow Environmental Observatory

ABSTRACT: Organic matter buried in Arctic soils and permafrost will become accessible to increased microbial degradation as the ground warms and remains unfrozen for longer periods due to climate change. The rates of organic matter degradation and the proportion of CH_4 and CO_2 greenhouse gasses released in a potential warming feedback cycle depend on the microbial response to warming, organic matter structure and availability, and the geochemistry of pH and electron transfer in pore water. To adapt and improve the representation of these Arctic subsurface processes in land models, we intensively examined soil organic matter transformations from middle, ridge and trough areas of a low-centered polygon on the Barrow Environmental Observatory (Barrow, Alaska). Significant amounts of iron(II) in organic and mineral soils of the active layer and groundwater indicate anoxic conditions. Unamended incubations of soils using relevant anoxic conditions at -2, +4 or +8 °C produced both CH_4 and CO_2, with different response curves. CO_2 formation followed Monod kinetics with a short initial lag. CH_4 production followed exponential kinetics, with a longer lag characteristic of microbial growth and adaptation. Rates of formation for both CH_4 and CO_2 were substantially higher in microcosms containing organic horizon samples (38-43% total carbon), compared to B horizon samples (17-18% carbon) or permafrost (16-18% carbon) that produced CO_2 but not CH_4 during incubations.

Measurements of ionic species dissolved in soil water from frozen cores, humic-rich surface water, or ground water extracted from the middle, ridge and trough in Sept. 2012 indicated low levels of nitrate and sulfate, constraining the role of these alternative electron acceptors in anaerobic respiration. The pH of surface water (4.4) was significantly lower than ground water (5.8 to 6.3). Substantial differences in other ionic species confirm that surface and ground water do not mix rapidly.

Biomass extracted from frozen mineral soil samples or thawed microcosms was analyzed for relative protein abundance using metaproteomics, and numerous peaks were matched to a database of Arctic genome data. Signature proteins from methanogenic archaea were identified in frozen permafrost and active-layer samples. After microcosm incubations, however, methanogenic proteins were found only in active-layer samples, consistent with headspace gas analyses. Therefore, low-centered polygon soil thawing and warming caused increases in microbial biomass and significant changes in microbial composition that determine the composition of greenhouse gas product mixtures. Differential microbial growth and migration through the thawing soil column may be key to changes in microbial population size and activity during prolonged thaw seasons. Microbial biomass production, fermentation, iron reduction and methanogenesis explain most of the C and electron flow in these closed systems.

NAME: Larry Hinzman
ORGANIZATION: University of Alaska Fairbanks
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Quantifying the Interactions of Geomorphic, Hydrologic and Thermal Processes to Improve Predictions of Climate Impacts and Feedbacks in the Arctic

ABSTRACT: The physical, chemical, and biological components of the Arctic are inter-related through a complex network of linkages, feedbacks and multi-dependent interactions. Theoretically a change in one variable in a part of the system can initiate a cascade of effects throughout the system, and these connections need to be understood and quantified in order to achieve improved predictability of climate impacts and feedbacks. The Next Generation Ecosystem Experiment, NGEE-Arctic, project has implemented a suite of coupled process observations within and near the Barrow Environmental Observatory in order to develop, initialize and evaluate high resolution process models that will be used to improve the land model component of the DOE-NSF Community Earth System Model, CESM. This landscape is a mosaic of thaw lakes and Drained Thaw lake Basins (DTLBs) characterized by ice-wedge polygons with a wide range of microtopographic properties. Given the very low relief and shallow thaw depth in this region, the microtopography associated with DTLBs and polygonal ground plays a significant role in the redistribution of wind blown snow, standing water, and soil moisture. These in turn impact the distribution of vegetation, soil temperature and soil biogeochemical properties and processes. Together these linked processes and attributes drive energy and carbon fluxes to the atmosphere.

A central theme of the NGEE-Arctic Hydrology and Geomorphology (HG) research focus area is to advance process understanding and prediction of climate-driven Arctic landscape evolution and its impact on Arctic hydrology and climate feedbacks. We are quantifying the interactions between geomorphic, hydrologic and thermal processes and how these processes control the spatial and temporal evolution of thermokarst, changes in microtopography, and the redistribution of soil water and temperature across the landscape. Field activities are being carried out across a gradient of polygonal ground (high-centered to low-centered polygons) nested within a DTLB age gradient. Data from the first year of NGEE-Arctic HG observations focused on measurement of snow depth, water levels, soil temperature, soil moisture and active layer depth at four sites with different ice wedge polygon micro-topographic configurations.

Preliminary results show the largest lateral fluxes of water are control by macro topography during snowmelt. However, micro-topographic differences in polygonal ground control small spatial scale differences in the distribution of snow, Summer precipitation, ponded water, soil moisture, soil temperature, vertical water fluxes and the timing and magnitude of runoff events. Thermal transect data show that at the start of Winter more snow and water accumulate in the ice-wedge polygon troughs and the low centers of the low-center polygons than on high-center polygons and polygon rims. This caused early freezing within the high-center polygons and rims, and prolonged freezing within the central depressions in low-center polygons. Hydrologic data show that polygon morphology significantly impacts seasonal water table height and water pressure gradients between polygon centers and trough networks. Variations in the frost table depth are more dramatic than the ground surface topography which impacts subsurface pathways. These data are now being used to inform high resolution thermal-hydrology and thermal erosion models which will help to parameterize processes for global land models.

NAME: Jitendra Kumar
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Multi-Scale Modeling of Eco-Hydrologic Processes in Arctic Ecosystems

ABSTRACT: Arctic and sub-Arctic ecosystems contain a vast amount of organic carbon stored within frozen soils. This environment is highly sensitive to climate change in a warming world, making the carbon stored in the frozen soil vulnerable to released to the atmosphere as CO2 and CH4 . Arctic ecosystems consist of complex and interconnected hydrologic, thermal, biogeochemical, geomorphic and vegetation processes. Any change or disturbance in any part of the system produces impacts on the entire system through complex process interactions and feedbacks. Model- and observation-based studies of these complex processes are required to understand and assess the impact of climate change on these sensitive environments. The Department of Energy’s Next Generation Ecosystem Experiments (NGEE‐Arctic) project is working to improve the Community Earth System Model (CESM) with process rich representation of Arctic ecosystems. We are developing a multi-scale modeling framework to model eco-hydrologic processes in the Arctic

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NAME: Brent Newman

ORGANIZATION: Los Alamos National Laboratory

PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Linking Permafrost Hydrology and Biogeochemistry: Using Stable Isotopes to Support Conceptual and Quantitative Modeling in the NGEE Arctic Project

ABSTRACT: As part of the DOE Next Generation Ecosystem Experiment – Arctic (NGEE-Arctic) project we are examining the lateral- and vertical- connectivity of water, nitrogen, and carbon systems in permafrost areas. Complex Arctic drainage networks can potentially lead to significant redistribution of water and biogeochemically important species over the landscape. Topographic features of arctic landscapes, especially polygonal ground, thaw ponds and lakes, comprise a complex and tortuous drainage network. In addition, a dynamic active layer and variations in soil- and ice-hydraulic properties act as important controls on vertical fluxes. Climate driven warming and degradation of permafrost may lead to changes in the low relief features as well as active layer thickness in low gradient regions like the North Slope of Alaska. Thus, it is necessary to develop a firm conceptual and quantitative understanding of the relationship between microtopography, larger-scale features such as rivers, and active layer dynamics to define and model how hydrological and biogeochemical processes feed-back to climate and Arctic ecosystems. In 2012 we conducted a synoptic isotope and geochemical survey at the Barrow Environmental Observatory (BEO) in Alaska. We tested a combination of methods including piezometers, drive points, and diffusion cells at multiple depths in the saturated zone and installed passive wicks and macrorhizons to sample the unsaturated zone. The analysis suite included cations, anions, DOC, TOC, DON, dissolved methane, and isotopes of water, DIC and DOC. Geochemical results show strong correlations with microtopographic units such as polygon type, and a wide range of redox conditions occur over the site. Thus, methane source and sink areas are likely strongly linked to these small-scale features. A limited set of samples from larger-scale hydrologic features such as major drainage channels shows significant chemical shifts from the small scale suggesting that it is important to understand multi-scale controls on where/how water is moving and the biogeochemical transformations that are occurring. Stable isotope data (^{2}H and ^{18}O) also show some important differences at the microtopographic scale indicating that water sources (e.g., rainfall or ice melt) and hydrological residence times can vary with depth and type of microtopographic unit. Carbon and nitrogen chemistry-and isotope-data demonstrate how biogeochemical cycling is strongly linked to the presence or absence of surface water ponding. For example, nitrogen production appears to be limited to high-centered polygons. High-centered polygons tend to develop more under degraded permafrost conditions. Thus, as degradation progresses, low-centered polygons become converted to high-centered polygons which could significantly impact nitrogen cycling and vegetation shifts in these Arctic systems. Overall, our findings suggest that the BEO system is a heterogeneous and dynamic hydrological and biogeochemical system with strong temporally- and spatially-driven variability at multiple scales.

NAME: Scott Painter
ORGANIZATION: NGEE
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Overview of NGEE Arctic Fine- and Intermediate-Scale Model Development

ABSTRACT: 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. An overview of the processes represented in the fine- and intermediate-scale models will be presented. Both models will represent non-isothermal surface and subsurface flows accounting for phase change using newly developed constitutive relations. Surface energy balance processes and carbon dynamics will also be represented. The fine-scale model will resolve microtopography at the scale of tens of centimeters horizontally with domain sizes of 100 m by 100 m. The computationally meshes for the fine-scale model will be derived from triangular surface meshes that track surface elevation and honor boundaries of individual ice-wedge polygons. These surface meshes are then extruded in the vertical direction to form prismatic elements. The intermediate-scale model is based on three grid cells per ice-wedge polygon, representing center, rim, and half-trough. The intermediate scale model uses the PFLOTRAN code and will use domains of size 10 km by 10 km in the horizontal. Development of the fine-scale model is proceeding on two tracks. Track 1 uses a static microtopography and the PFLOTRAN (Lichtner et al 2013) code. Track 2 will account for dynamic topography induced by ice-wedge thawing. Track 2 will use either PFLOTRAN or the Amanzi-ATS code (Coon et al. 2012).

Lichtner, P.C., Hammond, G.E., Bisht, G., Karra, S., Mills, R.T., and Kumar, J. (2013) PFLOTRAN User's Manual: A Massively Parallel Reactive Flow Code.

ET Coon, M Berndt, R Garimella, JD Moulton, and S Painter. A flexible and extensible multi-process simulation capability for the terrestrial Arctic. Frontiers in Computational Physics: Modeling the Earth System. Boulder, Co. Dec 2012.

NAME: William Riley
ORGANIZATION: Lawrence Berkeley National Laboratory
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Developing an improved CLM for high-latitude ecosystems: Above and belowground BGC, lateral subsurface hydrologic flow, and subsurface reactive transport

ABSTRACT: Current climate-scale land-surface models poorly represent many high-latitude processes important for accurate assessment of climate sensitivity. Recent analyses by our group and others have shown that, for example, the CMIP5 suite of models have a very wide range of predictions of high-latitude soil organic matter stocks, soil temperature profiles, and vegetation properties. To address these important shortcomings, the NGEE-Arctic project is working to integrate observations in a permafrost tundra region with several climate-scale model improvements in CLM. First, we have developed an optimization framework to improve representation of coupled plant carbon and nitrogen cycles. This framework seeks to optimize a specific set of plant processes (e.g., productivity, water use efficiency, nutrient use efficiency, transpiration) and reflects a particular competitive strategy a plant employs for survival, growth, defense, or reproduction. A new set of processes integrating multiple pathways of plant nitrogen uptake and associated plant-microbial interactions are incorporated as well as an improved representation of carbon and nitrogen allocation for plant parts and processes (e.g., photosynthesis and respiration). Second, we describe a subsurface reactive transport capability integrated with vertically-resolved C and N biogeochemistry that allows a consistent representation of the interactions between microbial activity, available nutrients, and soil mineral processes under different environmental controls, as well as the ability to directly compare vertically-resolved measurements with predictions. Third, we describe a capability, critical to the spatial scaling methodology being developed for NGEE-Arctic, of simulating lateral subsurface hydrological and tracer flows. CLM currently has a one-dimensional representation of subsurface flow and employs a non-unified treatment of hydrologic process in the vadose and phreatic zones. We implemented in CLM a variably saturated subsurface flow capability with lateral flows. We describe the hydrological and computational approach, present comparisons with analytical solutions, and present simulation results for idealized and actual watersheds.

NAME: Alistair Rogers
ORGANIZATION: Brookhaven National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Vc,max, Earth System Models and the Arctic

ABSTRACT: 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 CO_2 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). One of the key parameters required by the FvCB model is an estimate of the maximum rate of carboxylation by the enzyme Rubisco ($V_{c,max}$). In ESMs the parameter $V_{c,max}$ is usually fixed for a given plant functional type (PFT) and often estimated from leaf N content.

An investigation of the source of $V_{c,max}$ values used in ESMs revealed that despite representing the same PFTs, models were parameterized with a wide range of $V_{c,max}$ values (-46 to +77% of the PFT mean). Examination of models that linked leaf N content mechanistically to $V_{c,max}$ identified errors that would collectively decrease $V_{c,max}$ by 31% in C_3 plants. Only four ESMs currently have an Arctic PFT and the data used to derive $V_{c,max}$ for the Arctic PFT in these four models relied on small data sets and unjustified assumptions.

As part of a multidisciplinary project to improve the representation of the Arctic in ESMs (Next Generation Ecosystem Experiments - Arctic) we measured leaf N content and the response of photosynthesis (A) to internal CO_2 concentration (c_i) in order to determine $V_{c,max}$ for two sedges (*Carex aquatilis*, *Eriophorum angustifolium*), a grass (*Dupontia fisheri*), a forb (*Petasites frigidus*) and a shrub (*Salix pulchra)* growing on the Barrow Environmental Observatory, Barrow, AK. The values of $V_{c,max}$ currently used to represent Arctic PFTs in ESMs are 67% lower the values we measured in these species. Separate measurements of A made at ambient conditions in *Salix pulchra* and *Petasites frigidus* were compared with A modeled using the $V_{c,max}$ values we measured in Barrow, and those used by the ESMs. The A modeled with the $V_{c,max}$ values used by the ESMs was 77% lower than the observed A. When our measured $V_{c,max}$ values were used, modeled A was within 5% of observed A. Examination of the derivation of $V_{c,max}$ in CLM identified that cause of the relatively low $V_{c,max}$ value in CLM was the result of underestimating both the leaf N content and the investment of that N in Rubisco.

Here we have identified significant problems with the derivation of $V_{c,max}$ in ESMs that is relevant in all biomes, and provided new physiological characterization of Arctic species that is mechanistically consistent with observed CO_2 uptake. This new data can be used in future model projections to improve representation of the Arctic landscape in ESMs.

NAME: Vladimir Romanovsky
ORGANIZATION: University of Alaska Fairbanks
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Measuring and Modeling Changes in Permafrost Temperature at the UAF NGEE Arctic Permafrost Observatory in Barrow, Alaska

ABSTRACT: In 2001, a Permafrost Observatory was established within the Barrow Environmental Observatory in Barrow, Alaska under the auspices of the International Arctic Research Center of the University of Alaska Fairbanks. The observatory was established at the locations where permafrost temperatures were measured during the 1950s and early 1960s by M. Brewer of the U.S. Geological Survey to compare present permafrost temperatures with those obtained by M. Brewer. Those measurements were of very high quality, with a precision of generally 0.01°C. Comparison of permafrost temperature profiles obtained at the same location by Brewer on October 9, 1950 and by the UAF research group on October 9, 2001 shows that at the 15-meter depth (which is slightly above the depth of annual temperature variations) the permafrost temperature was warmer by 1.2°C in 2001 then in 1950. Since 2001, permafrost temperature at this depth increased additionally by 0.5°C. Most of this latest increase happened after 2005. Similar permafrost temperature dynamics during the last ten years was observed at the UAF Permafrost Observatories in the Prudhoe Bay region and could be explained both by an increase in air temperatures and in the snow depth at these locations. In 2012, the UAF permafrost observatory in Barrow was extended by installation of additional sensors at the three NGEE Arctic intensive research sites within the Barrow Environmental Observatory. The new installations allow establishing a two-dimensional view of the active layer and permafrost temperature dynamics at these locations.

A site-specific numerical model for the Barrow permafrost temperature regime was developed in the GI Permafrost Lab. The model was calibrated using data from shallow (down to one meter) soil temperatures obtained by K. Hinkel at a Barrow site with surface conditions similar to the Brewer site. No data from the Brewer sites were used for the calibration. Comparison of the modeling results and the Brewer's measured data shows an excellent agreement. The daily air temperatures and snow cover thickness during the entire period of measurements (1924-2011) at the Barrow meteorological station were used as input data for this calibrated model. As a result, a time series of daily ground temperatures for the depths between 0 and 200 meters were obtained. Analysis of this time series will be used in this presentation to reveal the effect of changes in air temperature and in snow depth on permafrost temperature and on the active layer thickness. Possible changes in these parameters as a result of the predicted changes in climate during the 21st century will be also presented.

NAME: Joel Rowland
ORGANIZATION: Los Alamos National Laboratory
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Use of high-resolution topographic and multispectral data to quantify and characterize polygonal ground attributes in Barrow, Alaska

ABSTRACT: Modeling of earth surface processes requires the discretization and characterization of the landscape. Discretization is needed to both define model grid cells and to characterize the properties and processes that govern landsurface dynamics. In the Next Generation Ecosystem Experiment (NGEE) – Arctic, we face the challenge of characterizing a unique and complex landscape currently not represented in Earth System Models (ESMs): polygonal ground on the North Slope of Alaska. A primary goal of NGEE is to improve climate simulations across model scales, from fine (less than a meter per pixel) up to coarse (on the order of 10 to 30 km) resolutions. For terrain with ice-wedge polygons, fine scale characterization is critically important because the processes that govern the carbon cycle and hydrological dynamics are controlled by landscape features on the order of a few to tens of meters. To characterize the polygonal ground in Barrow, Alaska we have combined remotely sensed data from high-resolution LiDAR-derived topography and Worldview 2 satellite imagery with subsurface data derived from geophysics and snow coverage data. Using the topographic data we have developed quantitative metrics that allow for the discretization and characterization of polygons. These metrics include standard topographic variables such as elevation, slope, curvature, and a novel "directed distance" metric. This analysis has allowed us to delineate polygon boundaries, discriminate individual polygon features (rims, troughs, and centers), and broadly classify polygons into types (high versus low). These efforts enable the generation of high resolution modeling grids (pixels ~ 0.25 m) that capture the actual Barrow topography and coarser resolution grids based on a synthetic representation of polygon attributes. In addition to model grid development, we have been able to use distributed measurements of topographic properties and multispectral data to extrapolate point and transect based geophysical data of the subsurface and snow distribution to make landscape-scale predictions of active layer thicknesses (ALT), soil moisture, and snow distribution. Using data fusion approaches, we have successfully developed a methodology for combining topographic metrics with Normalize Difference Vegetation Index (NDVI) and probe measurement of ALT to predict ALT values across our model domain. Similarly, using topography and snow depth measured by point probes and ground penetrating radar we are able to make an estimate of snow depth distributions across the polygonal network accounting for the effects of microtopographic features on the snow redistribution and accumulation. These examples highlight the potential for coupling remotely sensed dataset with ground based observations to discretized, parameterize, and test both fine and medium resolution land surface models in polygonal terrain.

NAME: Victoria Sloan
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Using vegetation and soil characteristics to inform model scaling of a polygonal tundra landscape

ABSTRACT: In complex, heterogeneous landscapes such as polygonal tundra, identification of distinct vegetation communities according to their structural and functional characteristics is essential to determine the approach to fine-scale model parameterizations. Further, linking these communities to observable geomorphic units in the landscape provides a key mechanism for scaling from plot-level measurements to the broader grid-cell scale used in climate models.

During July 2012, vegetation community composition was determined in 48, 1 m^2 plots located on the centers, rims and troughs of low-centered, high-centered and transitional polygons in the polygonal tundra of the Barrow Environmental Observatory (BEO), Barrow, Alaska. Vegetation and soil characteristics (e.g. plant biomass, plant height, leaf area index, plant tissue chemistry, nutrient availability, soil moisture, Soil temperature and thaw depth) were measured at the same locations.

One-way cluster analysis identified four vegetation communities in the study area: i) tall *Carex* (sedge) dominated communities, ii) mixed tall graminoid-forb-moss communities, iii) dry graminoid-lichen communities and iv) low-stature, lichen dominated-communities. These groupings were confirmed by non-metric multidimensional scaling (NMDS), which also showed that the dominant environmental gradients relating to community composition were soil moisture (R^2 = 0.75) and soil NH_4 availability (R^2 = 0.65), though these variables were not independent. The four groups mapped clearly to micro-topographic position, corresponding with i) low centers ii) troughs, iii) rims and transitional polygon centers, and iv) high centers.

Comparison of this vegetation classification with a 10-group unsupervised landscape classification from high resolution multi-spectral data (Worldview2) showed good correspondence in some, but not all, areas. This indicated that this is a promising approach for scaling from point measurements, but that further refinement of both vegetation and landscape classifications could prove useful.

Overall, this analysis identifies four key units to resolve in geomorphological analyses of the BEO, and presents a framework for parameterizing of fine-scale models (e.g. TEM-DVM) for the intensive study areas associated with the Next Generation Ecosystem Experiments (NGEE) in the Arctic. Future work will include incorporating additional soil variables into the classification, and determining the extent to which soil and vegetation classifications are coupled.

NAME: Lydia Smith
ORGANIZATION: University of California Berkeley
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Process-level controls on greenhouse gas emissions in Arctic coastal tundra

ABSTRACT: According to current estimates, permafrost soils store more than two times the carbon as the carbon in atmospheric CO_2. With climate change causing high latitude soils to warm and dry, this soil carbon will likely become more available to decomposition. The magnitude of these predicted carbon emissions as CO_2 and methane (CH_4) are poorly constrained due to several factors, including fine-scale environmental heterogeneity, unknown and complex controls on microbial processes, and uncertainty in carbon stocks and current emissions rates. This work aims to improve our ability to predict Arctic greenhouse gas fluxes from the cm- to the landscape-scale by investigating the biological and environmental controls on CO_2 and CH_4 production, consumption, and emissions. On the Arctic coastal plain in Barrow, Alaska, we combine a suite of biogeochemical measurements beginning in 2012 and extending through 2013. We measure in situ trace gas fluxes using static chambers and eddy covariance towers across a range of landscape features; greenhouse gas concentrations in soil pore space and stable and radioisotopes throughout the soil depth profile; soil physical data such as temperature and moisture at depth; and vegetation greenness using normalized difference vegetation index (NDVI). In laboratory experiments with soils collected on site and incubated at two temperatures, we measure CH_4 and CO_2 flux and the radiocarbon content of respired CO_2 and bulk soil. Initial results from 2012 indicate that landscape polygon feature, soil water content, soil temperature, and sampling location all influence CO_2 and CH_4 fluxes. Soil CO_2 fluxes measured with static chambers decreased toward the end of the growing season, whereas CH_4 fluxes remained constant or increased. From half-hourly eddy covariance data between September and October 2012, net ecosystem exchange ranged between -0.02 and 0.10 g C m^{-2}, and maximum evapotranspiration and CH_4 flux were 0.03 mm, and 50 mg CH_4 per half hour respectively. NDVI values correlate well with microtopographical polygon features. Stable isotope measurements indicate methane production in deeper and wetter soils, with increasing methane oxidation toward the soil surface, dependent on polygon feature. ^{14}C data show that CO_2 respired from deep soils is very old relative to surface soils. Taken together, along with ancillary microbial, geophysical, hydrological, and vegetation data from collaborative research teams, our results suggest that soil moisture is a major control on carbon cycling processes, with interacting environmental and biological effects. Continued research through 2013 will further investigate the vulnerability to climate change of this region's old carbon stores.

NAME: Neslihan Tas
ORGANIZATION: LBNL
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Microbial ecology across polygon features at the NGEE-Arctic Barrow site

ABSTRACT: Arctic soils contain an estimated 12-42% of terrestrial carbon, most of which is sequestered in permafrost. As the permafrost thaws due to global warming, the trapped carbon can potentially be degraded by microbial activity resulting in greenhouse gas (GHG) emissions. On the Alaskan North Slope the collapse and rise of soil due to formation of ice wedges and permafrost thaw create distinct features called polygons. As part of the DOE Next Generation Ecosystem Experiment (NGEE) in the Arctic, we aimed to determine the horizontal and vertical distribution of microbial populations in the polygon features and to determine the potential for GHG emissions due to microbial processes. To determine the horizontal microbial distribution we collected seasonally thawed active layer soil samples along a 500 m transect of polygons (Barrow site 0), including high-centered, transitional and low-centered polygons. In addition, two deep cores (1 m and 3 m depth) were taken from a transitional polygon in the same transect. Prior to sectioning, the cores were CT-scanned to determine the physical heterogeneity throughout the cores. The microbial community compositions along the horizontal transect and in the deep cores were determined by high throughput and deep sequencing of 16S rRNA genes and metagenomes. The sequence data was correlated to GHG flux measurements, geophysical and geochemical soil characteristics. The microbial community composition varied both horizontally and vertically along the polygon transects. Differences in elevation and moisture content were identified as the main drivers of the observed changes. Both the genes for methanogenesis and CH_4-flux measurements were higher in low-centered, wetter polygons compared to high-centered, drier polygons. By contrast, CO_2 production was more prevalent on the ridges of the polygons and in the high-centered polygons. The metagenome sequence data also revealed that the pathway for utilization of nitrate as a nitrogen source was present in the polygon features, but not the complete pathway for denitrification; suggesting that N_2O production capacity was limited. There were also dramatic shifts in community with depth based on profiles obtained from the deep 1m and 3m cores. In the upper layers there were sequences corresponding to Verrucomicrobia (potential methanotrophs) and Acidobacteria. Actinobacteria were more abundant in the mid layers, whereas sequences corresponding to methanogens were abundant in the deeper permafrost layers. To date we have obtained 12 novel isolates from deep layers of the 1 m core, including isolates belonging to fermentative *Clostridia*, *Sporosarcina* spp. and iron reducing *Rhodoferax* spp. as well as several methanogens that grew and produced methane at 2°C. The isolate genomes are currently slated for sequencing at JGI.

NAME: Stan Wullschleger
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Advanced Characterization of Active Layer and Permafrost Variability using Geophysical Approaches

ABSTRACT: The arctic tundra ecosystem is recognized as a large source of uncertainty in quantifying feedbacks to global climate warming. Improving understanding of arctic ecosystem functioning and parameterizing process-rich models that simulate feedbacks to a changing climate require advances in estimating the spatial and temporal variations in active layer, ice-wedge and permafrost soil properties. In the context of the Next-Generation Ecosystem Experiments (NGEE-Arctic), we worked on the development of advanced geophysical strategies to improve arctic subsurface imaging and monitoring, as well as understanding interactions between soil properties and arctic ecosystem processes and dynamics. Some specific objectives involved improving (i) geophysical capability in characterizing different subsurface features, including active layer, ice-wedges, ground-ice, saline layers, and permafrost with variable ice-content, (ii) quantifying relations between soil-geochemical properties, geophysical, and geomorphological properties, (iii) integration of multi-scale and -resolution geophysical and point measurements, (iv) strategies to monitor freeze-thaw and water dynamics, and (v) estimates of properties (such as thaw depth, soil moisture, snow depth and water equivalent, ice content and geochemical parameters) and their uncertainty over scales that are relevant for modeling. These objectives were pursued through various numerical developments, laboratory experiments, and field investigations. Field investigations have been performed at the NGEE site located in the Barrow Environmental Observatory (BEO) near the coastal village of Barrow (AK), which is dominated by different types of ice wedge polygons. Acquired geophysical measurements include complex resistivity or electrical resistivity tomography (ERT), electromagnetic induction (EMI) data using portable tools, multichannel analysis of surface waves (MASW) seismic data, ground-penetrating-radar (GPR) data, and time-domain reflectometer (TDR) data. Petrophysical, geochemical, snow point measurements, as well as airborne LiDAR data were used to constrain the interpretation of the geophysical data.

Our major recent advances include (i) a novel parameter-estimation approach adapted to explore the solution non-uniqueness inherent to EMI data and importantly to estimate quickly both electrical conductivity variations in the active layer and trends in permafrost distribution over large areas as enabled by the extensive spatial coverage of EMI data, (ii) an unconventional full-waveform method for MASW data that is especially suitable for resolving low seismic-velocity features that may be associated with permafrost soils with abundant unfrozen water, (iii) high-resolution imaging of ice-wedges, permafrost and active layer using multi 2D ERT at a high-spatial resolution that enables identification of properties that vary substantially over length scales of less than a few meters, (iv) understanding the complex resistivity electrical signature of the freeze thaw states and transitions of arctic soils trough column experiments that will serve for setting field monitoring, (v) an advanced hierarchical Bayesian model for integrating multiscale, multi-type point/geophysical/remote-sensing datasets that provide estimates of subsurface properties and their associated uncertainty, and (vi) identification of relations between subsurface properties and surface properties that can serve for zonation at larger scales and/or parameterization of mechanistic models. The above developments will facilitate the identification and modeling of critical terrestrial ecosystem characteristics and behaviors.

NAME: Natalie Griffiths
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Spatial and temporal variation in peat pore water chemistry of a northern peatland: Reference conditions of a large-scale climate change experiment (SPRUCE)

ABSTRACT: Climate change will disproportionally affect higher-latitude ecosystems, and northern peatlands will be particularly susceptible. Decomposition in these high-carbon ecosystems is expected to increase in a warmer, carbon dioxide enriched future. Quantifying the dynamics of carbon and associated biogeochemical cycles under current and future climate scenarios is necessary to understand how climate change may alter these important ecosystem processes. During a large-scale ecosystem experiment in an 8.1-ha black spruce-*Sphagnum* bog at the Marcell Experimental Forest (Marcell, MN), temperature (ambient to +9 °C) and CO_2 concentrations (ambient, +900 ppm) will be increased inside replicated, 12-m diameter, open-topped chambers. Prior to the onset of this experiment, we measured the spatial and temporal variation in peat pore water chemistry to develop a baseline for the design of the experiment and to better understand biogeochemical cycling under ambient conditions. We found the largest differences in chemistry by depth (0 to 3-m deep), and little variation in near-surface pore waters from bog, lagg (transitional zone between uplands and the bog), and outlet stream. Ammonium was low at the surface (0.1 mg/L) likely due to plant uptake, but was highest at depth (3.8 mg/L), potentially due to remineralization in the absence of nitrification. Nitrate was almost always undetectable, except in near-surface layers during snowmelt when the water table is high and nitrate bypasses plant and microbial uptake before being exported. Total organic carbon decreased from surface (60 mg/L) to deep (20 mg/L) peats, yet concentrations were at least an order of magnitude higher than in most well-studied upland ecosystems. Phosphorus in deeper peats was also high, but there was significant variation in space and time. Overall, there are two different pools of water within the peat: shallower waters originating from precipitation, and deeper waters originating from long residence times in the peat and exchange with the regional groundwater aquifer. If increased temperature results in greater evapotranspiration and drier conditions, these previously-isolated deep ammonium and phosphorus pools may become available, with cascading effects to plant and microbial communities.

NAME: Lianhong Gu
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Photosynthetic Activity and Net Carbon Uptake in a Drought-Prone Temperate Deciduous Forest

ABSTRACT: Canopy function greatly influences carbon relations in forest ecosystems. Changes in photosynthetic capacity of foliage as well as leaf area and environmental constraints during the growing season can greatly alter canopy function and carbon uptake by photosynthesis. These attributes have received some study (e.g., Wilson et al., 2000), but there has been little comprehensive study of seasonal patterns of leaf function from the perspective of morphology, biochemistry and environmental constraints at the canopy scale. We studied canopy structure and function during two growing seasons with wide variation in climatic conditions, particularly in soil moisture availability. Dominant species at the site (white oak, *Quercus alba* L., black oak . *Q.velutina* Lam., shagbark hickory, *Carya ovata* Mill, sugar maple, *Acer saccharum* Marsh. and eastern redcedar, *Juniperus* v*irginiana* L.) were chosen for study. We found that inter-annual variation in net carbon uptake at this deciduous forest site is substantial and can vary by a factor of more than two on a decadal scale. Meteorological drought (and its absence) appears to play a dominant role in control of the carbon cycle at MOFLUX.

NAME: Lianhong Gu
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Use of MOFLUX data to advance ecosystem process understanding and improve global carbon cycle models

ABSTRACT: The Missouri Ozark forest AmeriFlux site (MOFLUX) is strategically located in an ecologically important transitional zone between the central hardwood region and the central grassland region of the US. Since the initiation in 2004, measurements made at this ecotonal site have yielded crucial insights into the dynamics of terrestrial flux exchanges with the atmosphere and the physical and biological processes controlling such dynamics. A wide spectrum of drought regimes have occurred at MOFLUX, providing excellent opportunities for understanding water controls on ecosystem functions and for testing model drought responses. MOFLUX also supports fundamental processed-based measurements and analyses that have been led to improvements of carbon cycle models. In this poster, we summarize the use of MOFLUX data to advance ecosystem process understanding and improve global carbon cycle models.

NAME: Paul Hanson
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Peatland microbial responses to moisture manipulation in laboratory mesocosms

ABSTRACT: The unique microtopography of sphagnum bogs often results in the co-occurrence of elevated, moist hummocks and well saturated hollows of variable size and plant composition. These environmental differences may also result in spatially distinct microbial and invertebrate communities and function. The Spruce and Peatland Under Climate and Environmental Change (SPRUCE) project will be a temperature and CO_2 manipulation experiment in an ombiotrophic bog in the Marcell Experimental Forest, MN that features such hummock/hollow topography. We anticipate warming will alter plot water balance and lead to a strong declines in hummock moisture and moderate declines in hollow moisture. We were interested how microorganisms in well saturated hollows respond to moisture stress compared to the drier hummocks. In this mesocosm incubation study we sought to initially determine how microbial and invertebrate communities, enzyme activity and respiration in hummock and hollows would change following exposure to simulated moderate and severe drought without confounding warming effects.

In October, 2012 two 20x20x20cm sections of peat, hummock and hollow, were collected from the Marcell Experimental Forest, MN and divided into 15 hummock mesocosms and 24 hollow mesocosms. The mesocosms were maintained at one of three moisture regimes; ambient, 75% of ambient, and 50% of ambient to simulate different drying scenarios. Peat mesocosms were incubated at room temperature in quart mason jars for 112 days and on days 2, 13, 42, 91 and 112 days post drying we measured 1) exoenzyme activity, 2) bacterial, fungal, archaeal, and invertebrate abundance measured by qPCR, 3) microbial biomass measured with fumigation/extraction, 4) and dissolved organic carbon. Seven hydrolytic enzymes, involved in C, N and P cycling, and two oxidative enzymes were used in enzyme assays. In addition, respiration measured as CO_2, was monitored throughout the incubation.

The hummock and hollow peat mesocosms responded differentially to the drying scenarios, with the hollow microbial communities most affected by moisture. The hollow samples exposed to a 50% moisture reduction resulted in a decline in six of seven hydrolytic activities within two days of drying. This reduction was maintained throughout the experiment for three N-enzymes, one C and P enzyme. In the hollow mesocosms, there was also a decline in fungal gene copies with drought in the first 13 days following dry-down. In hummock samples, activity in the two peptidase enzymes increased under drought, while other microbial metrics, oxidative enzymes and microbial gene copy numbers, were unaffected by moisture treatment. Total respiration was similar between moisture treatments in the first 26 days following drying, however there was twice as much CO_2 respired from hummock mesocosm compared to hollows. Invertebrate analyses are still ongoing at this time. Overall, hummock microbial communities and function were largely unaffected by moisture stress perhaps suggesting their communities are adapted to the more variable moisture levels experienced in the native bog environment.

NAME: Paul J. Hanson
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: ORNL's Terrestrial Ecosystem Science Scientific Focus Area

ABSTRACT: 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 CO_2 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 ongoing Spruce and Peatland Responses Under Climatic and Environmental Change (SPRUCE) experiment are conducted to quantify biogeochemical responses to environmental and atmospheric change variables 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. Additional process research and landscape-scale, carbon-cycle observations in understudied ecosystems improve 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.

NAME: Paul J. Hanson
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Evaluating high-carbon peatland responses to environmental change: a report on pre-treatment C stocks and fluxes for a characteristic ombrotrophic bog and projected response to warming by elevated CO2 treatments

ABSTRACT: Identification of critical environmental response functions for terrestrial organisms, communities, and ecosystems to rapidly changing climate conditions are needed to evaluate ecological consequences and feedbacks. We are constructing an experimental platform to address climate change response mechanisms in a Picea/Larix/Sphagnum ombrotrophic bog ecosystem located in northern Minnesota. This ecosystem located at the southern extent of the spatially expansive boreal peatland forests is hypothesized to be especially vulnerable to climate change and to have important feedbacks on the atmosphere and climate. Preparations are being made for a replicated experiment to test mechanisms controlling vulnerability of organisms and ecosystem processes changes for multiple levels of warming (up to +9°C) combined with elevated CO2 exposures (900 ppm).

Through the execution of this experiment we will quantify changing greenhouse gas emissions to the atmosphere, thresholds for organism decline or mortality, limitations to regeneration, and biogeochemical limitations to productivity. The experiment will allow for the evaluation of responses across multiple spatial scales including: microbial communities, bryophyte populations, various higher plant types, and some faunal groups. Direct and indirect effects of these experimental perturbations will be tracked and analyzed over a decade for the development and refinement of models needed for full Earth system analyses.

Pretreatment simulations of anticipated ecosystem responses to the range of warming and elevated CO_2 treatments have been undertaken. Those simulations shed light on important interactions taking place between primary carbon cycle processes and productivity driven changes in element cycles that allow for fertilization of the dominant vegetation. Long-term carbon cycle changes in such high-carbon systems will be driven by the success or failure of a all vegetation types, but the interplay between Sphagnum communities at the ground surface vs. the success of overtopping shrub and tree species will drive long term community composition and net C flux.

NAME: Paul J. Hanson
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Long-term Experiments and Observations: Fertile Ground for Model Benchmarking and Improvement In the Context of Environmental Change

ABSTRACT: The DOE Office of Science Biological and Environmental Research (BER) program is a key supporter of fundamental research to understand ecological effect of environmental change. Recent and ongoing research in this area provides an understanding of how climatic and atmospheric changes can modify the form and function of terrestrial ecosystems. A number of BER's long-term observations and manipulations are being used to evaluate, parameterize and hopefully improve ecosystem models. Key results from several other BER-funded studies are highlighted as potential fodder for future model-experiment-observation interactions.

For example, long-term support of elevated carbon dioxide (CO_2) exposure studies in a range of ecosystems demonstrated enhanced terrestrial carbon uptake into both plant biomass and soil carbon pools. The uptake capacity, has however, been shown to be reduced when nutrient limitations or water stress become key constraints. Long-term and large-scale precipitation manipulations designed to induce severe drought have revealed a tremendous contrast between the resilience of trees in wet eastern ecosystems and their vulnerability in dry western environments. Warming studies, both completed and ongoing, demonstrate a complex mixture of responses, including extended annual growth periods and enhanced nutrient mineralization resulting in increased plant growth. Such arguably beneficial responses are contrasted with warming-induced losses of important greenhouse gases to the atmosphere (CO_2 and methane) and the acceleration of drought conditions. BER has also pioneered studies to apply state-of-the-science technologies, molecular analyses, and genetic methods to the evaluation of ecosystem-scale responses to climatic and atmospheric changes. All of this research produces important lessons-learned that should be reconciled against the predictive capacity of available ecosystem models. <u>Are such lessons being transferred to the model-projection activities?</u>

Models' predictive capacity stems from the presence of fundamental mechanisms and important structural relationships within prognostic models. The absence of key mechanisms within ecological models undermines their capacity to provide policy-relevant predictions of both climate change impacts and future greenhouse gas trajectories from those ecosystems. Future model-experiment-observation should be fostered to improve a wide range of ecosystem. Through the development of an integrated understanding of multiple, interacting environmental effects (i.e., structured models), the scientific community can generate viable prognostic models to inform policy makers and the public about the capacity of ecosystems to provide goods and services for society under projected rapid rates of climate change.

NAME: Les Hook
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: ORNL's TES SFA Data and Model Management and Archiving to Enhance Model-Experiment-Observation Interactions

ABSTRACT: 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 identifying 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 (e.g., http://tes-sfa.ornl.gov/) and data center archived products 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).

This poster highlights ORNL TES SFA tasks, representative data products, and their availability to project staff and the public.

NAME: Colleen Iversen
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: The distribution and dynamics of fine roots in a forested bog in northern Minnesota, USA

ABSTRACT:

Research objectives

We initiated an experiment to determine the distribution and dynamics of ephemeral roots in an ombrotrophic bog that is the future location of the Spruce and Peatland Responses Under Climatic and Environmental change (SPRUCE) experiment. Minirhizotrons, a technology that is rarely used in wetlands, provided an opportunity to examine ephemeral roots in an important and understudied ecosystem.

We used several methods to characterize the distribution and dynamics of ephemeral roots in the bog. We gathered an international team of minirhizotron and wetland experts and developed a consensus on, and a methodological framework for, the appropriate installation and use of minirhizotron technology in wetland ecosystems (Iversen et al., 2012, *Plant and Soil*). In July, 2010, we installed minirhizotrons across gradients of tree density and microtopography in the bog. We collected images from the minirhizotrons weekly throughout the growing seasons of 2011 and 2012 to quantify root production, mortality, and depth distribution dynamics. During the same time period, we tracked the growth of adjacent trees using automated and manual dendrometers. Last, we investigated the relationships among root order, root morphology, and root chemistry for common bog species to scale minirhizotron data to ecosystem carbon and nitrogen fluxes.

Results/Plans

We found that: (1) Minirhizotron technology allowed the quantification of ephemeral root dynamics in a bog and should be utilized in other wetland systems. (2) Root standing crop increased quickly in the spring, well before wood growth was initiated, and standing crop was lowest in areas of ‘low’ tree density that characterize many of the future SPRUCE experimental plots. (3) Bog surface microtopography exerted strong controls over root dynamics. Root standing crop and production were much greater in raised hummocks when compared with saturated hollow depressions. (4) The most common vascular plant species in the bog encompassed a range of root morphology and diameter distributions, as well as mycorrhizal colonization. Across a range of root orders, root diameter was strongly related with root mass per length and root nitrogen concentration.

Measurements taken prior to the SPRUCE experimental manipulation will be used to parameterize ecosystem and land surface models to refine hypotheses regarding the expected effects of warming and elevated CO_2 on ecosystem carbon and nitrogen cycling in the forested bog. This combined measurement and modeling approach will improve our understanding of root distribution, dynamics, and carbon and nitrogen cycling in globally important peatland ecosystems.

NAME: Jiafu Mao
ORGANIZATION: ORNL
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Evaluation and Development of CLM based on PiTS and EBIS observations

ABSTRACT: The Partitioning in Trees and Soil (PiTS) project at ORNL was established to improve the parameterization of C partitioning routines in existing ecosystem models by exploring mechanistic model representations of partitioning tested against field observations and manipulations. The Enriched Background Isotope Study (EBIS) experiment was designed to use unique ^{14}C-enriched materials to characterize the rate of C flux from litter sources to mineral soil sinks over a range of climatic and biological conditions. These two existing field data sets at ORNL provide a unique opportunity for the evaluation, calibration and development of ecosystem models particular the Community Land Model (CLM) supported by the U.S. Department of Energy (DOE). In this presentation we will report our ongoing work to set up the CLM simulations and improve the model performance at these two sites. In addition, we will discuss future directions bettering the observation and CLM development based on these experiment-model integrations.

NAME: Melanie Mayes
ORGANIZATION: ORNL
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Development and Testing the Microbial ENzyme Decomposition (MEND) Model

ABSTRACT: Contemporary models of soil organic carbon simulate C dynamics by determining pool sizes and turnover rates *post hoc* from long term agricultural experiments. This standard representation does not explicitly consider microbial activities, and this lack of quantification means that acclimation of the heterotrophic community and associated exo-enzyme activities to climate change and edaphic conditions are ignored. We created a mechanistic microbial model of enzymatic degradation of measureable pools of soil organic C (OC), the Microbial-ENzyme-mediated Decomposition (MEND) model. The pools consist of soil OC as mineral-associated OC (< 53 µm), particulate OC (> 53 µm), dissolved OC and sorbed dissolved OC, and microbial biomass. Particulate OC is separated into major categories of plant matter (cellulose, lignin) that are attacked by different major classes of microbial enzymes. The activities of extracellular enzymes are considered through the Michaelis-Menten equation, and the model is parameterized by steady-state and dynamic analyses using kinetic parameter values and pool estimates gleaned from an extensive literature search. Lab-scale sorption and incubation experiments using four different ^{14}C labeled substrates (glucose, cellulose, lignin monomer, and fatty acid) and a global selection of soils are being used to calibrate the model. Model sensitivity analysis identified microbial growth efficiency, enzyme production rate, and microbial maintenance rate as targets for current experimental endeavors. Microbial growth efficiency is emerging as an important, temperature-sensitive adjustment of microbial physiology. Several publications predict that growth efficiency decreases as temperature increases, which resulted in lower CO_2 fluxes from the MEND model when compared to constant growth efficiency. Current lab experiments involve testing the growth efficiency under a variety of conditions. For future model testing and field-scale verification, we will choose field sites including tropical, temperate, and arctic ecosystems to determine the functional and phylogenetic composition of the microbial community and its contributions to carbon and nutrient cycling. Eventually, we will link MEND into the Community Land Model (CLM4) and compare performance with the existing model structure. The ultimate outcome is a validated, realistic, globally-relevant mechanistic microbial soil OC model as a robust and mechanistic component of land-surface models in global climate and earth system models.

NAME: Daniel Ricciuto
ORGANIZATION: Oak Ridge National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Modeling the terrestrial carbon cycle at regional to global scales: Parameter sensitivity and evaluation against benchmarks

ABSTRACT: Despite increased mechanistic complexity, terrestrial carbon cycle models continue to exhibit large variability in predictions of both present and future carbon fluxes. While a portion of this variability is a result of differences in model structure, both uncertainty and spatial variability in model parameters also play a large role. Model parameter calibration studies to date have primarily focused on improving models using observations from individual flux tower or experimental sites. While these studies re valuable for testing model response and for local model improvements, it remains unclear whether these optimized parameters can be used to improve predictions consistently over large regions. A wealth of observations at multiple scales from remote sensing and upscaled data products from observation networks are now available. These observations have the potential to greatly constrain carbon cycle model parameters and predictions. However, many of these datasets have typically been used so far for validations and not to explore structural and parametric uncertainty in a formal way. The Multi-Scale Synthesis and Terrestrial Mode Intercomparison (MsTMIP) project is beginning to answer questions about the impacts of model structure on the simulated carbon cycle using several of these global-scale datasets. Primary limiting factors for such global model analyses are high computational demand and complex cyberinfrastructure involved in performing multiple simulations and processing output. Here we present frameworks for global ensemble carbon cycle simulations using the Global Terrestrial Ecosystem Carbon (GTEC) model and the Community Land Model (CLM-CN) at 0.5 degree spatial resolution using standardized datasets provided by the MsTMIP team. We use these single model ensembles to explore uncertainty and model performance against the FLUXNET network, remotely sensed leaf area index (LAI), and biomass datasets. We also use the ensemble simulations to quantify uncertainties in key parameters and predictions.

NAME: Xiaoying Shi
ORGANIZATION: ORNL
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Development and testing the hydrological dynamics of vegetated wetland for CLM

ABSTRACT: The SPRUCE project has engaged several modelers to produce a priori model projections of the experimental treatment conditions to rationalize magnitudes of responses within the SPRUCE experiment. To represent vegetated wetlands in community Land Model (CLM), we incorporate key structural and process changes in the model. Initial efforts with CLM have focused on model modifications needed to represent the isolated hydrologic cycle of the bog environment, as well as the observed patterning of the bog interior into raised hummocks and sunken hollows having distinct hydrologic dynamics and vegetation communities. The preliminary results from the hydrological efforts show that seasonal hydraulic dynamics (water table depths for the hummock/hollow topography) are reasonable and comparable to the observation. Next steps for a priori CLM modeling are to couple the new hydrology treatment with vertically structured soil organic matter pools, and then to introduce components of a methane model recently developed for CLM.

NAME: Anthony Walker
ORGANIZATION: Oak Ridge National Lab
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: FACE experiment model inter-comparison synthesis.

ABSTRACT: A wealth of data on forest ecosystems have been gathered at free-air CO_2 enrichment (FACE) experiments. The spatial and temporal scales over which these data were collected make the FACE experiments ideally suited for comparison with terrestrial biosphere models (TBMs) and in this study we simulate the Duke and Oak Ridge forest FACE experiments with a suite of 11 TBMs.

Introducing confidence intervals to model-to-observation goodness-of-fit (GOF) metrics demonstrated that only a single model (which was heavily parameterised) was a statistically better predictor of annual net primary production (NPP) under ambient CO_2 than the mean of those observations. However, many more models captured a significant level of the inter-annual variability in NPP and the reason for the poor comparison with the observed mean as a predictor was either due to a positive magnitude bias or a lack of sensitivity to drivers of inter-annual variability (low sensitivity bias).

We advocate a diagnosis of the under-lying causes of differences between the models, followed by assessment of these competing model structural assumptions (hypotheses) in the context of observed/experimental data. Applied to the simulation of leaf area index (LAI) the competing hypotheses represented by the model structural assumptions are classified by their partitioning of leaf carbon (fixed-scaling, pipe-model or optimisation) and leaf growth and litterfall phenology (none, active, multi-phase).

Poor reproduction of the evergreen seasonal LAI cycle demonstrated that fixed-scaling or the pipe-model without active litterfall phenology were inconsistent with the observed data. A major difference between the various modelling methods was the timelag between carbon assimilation and incorporation into leaf growth and the timing of the determination of LAI (instantaneous or a seasonal delay). Observations potentially support the pre-determination of a 'target' LAI although further research needs to be done to understand the underlying determinants of LAI versus the constraints on LAI.

NAME: Dali Wang
ORGANIZATION: ORNL
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: A high performance data platform for terristrial ecosystem modeling

ABSTRACT: Significant progresses have been made on key components of terrestrial ecosystem sciences, i.e., experiment, observation, and model. However, the multidisciplinary integration has been generally left behind. This poster presents some of our current efforts towards a high performance data platform to advance integrated ecosystem sciences. Based on two-tier software architecture, this data platform, which leverages high performance computing capability and adopts the fundamental of Geographic Information System (GIS) design, is to provide interactive ecosystem manipulation capability for direct measurement-model connection, realistic landscape representation, and large scale phenomena diagnostic analysis for decision making. Specifically, three cases have been presented; they are 1) CLM functional unit testing on photosynthesis; 2) landscape categorization based on temporal-spatial datasets analysis and clustering; as well as 3) a global CLM offline simulation diagnostic analysis on HPC platform. Innovative computational methods using the ORNL Leadership Computing Facility (OLCF) will also be discussed to address technical challenges associated with those exemplary scenarios and several future efforts.

NAME: Xiaojuan Yang
ORGANIZATION: Oak Ridge National Lab
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Modeling P dynamics and P limitation on productivity in tropical forests

ABSTRACT: One of the major uncertainties in the prediction of future carbon(C) uptake and storage comes from the treatment of carbon-nutrient interactions in global C-climate models. Phosphorus (P), the most limiting nutrient in tropical regions, has yet to be incorporated into global C-climate models (except for CASA-CNP and JSBACH). Here we introduce P dynamics and C-N-P interactions into the CLM4-CN model and investigate the role of P cycling in controlling the productivity of tropical ecosystems. The newly developed CLM-CNP model includes all major biological and geochemical processes controlling P availability in soils and the interactions between C, N, and P cycles. The model is first evaluated against measurements from four sites along a Hawaiian soil chronosequence. Preliminary results indicate that the introduction of P limitation greatly improved the model estimated NPP. The modeled vegetation and soil organic C, N and P as well as inorganic P pools compare well with the observations. The model is also able to predict the shift in nutrient limitation along this chronosequence (from N limited, to N-P co-limited, to P limited). We also apply the CLM-CNP model at five intensively studied RAINFOR sites in the Amazon watershed to evaluate the model performance against the observations and investigate how P status affects above ground productivity in tropical forests. These site level simulations improve our understanding of how P dynamics affect terrestrial C dynamics. The evaluations against site-level observations increase confidence in applying the model more broadly to regional and global scales.

TERRESTRIAL ECOSYSTEM SCIENCE

PACIFIC NORTHWEST NATIONAL LABORATORY (PNNL)

NAME: Vanessa Bailey
ORGANIZATION: Pacific Northwest National Laboratory
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Reduced soil microbe resilience and respiration after a 17-year climate change experiment

ABSTRACT: Climate change is predicted to profoundly perturb the fundamental processes controlling the balance between soil C accrual and mineralization across landscapes: both reaction rates and products may be affected. To assess the effects of changing climate on soil C cycling, we re-sampled an existing reciprocal soil transplant experiment that was initiated in 1994 at the Arid Lands Ecology Reserve (WA). At that time, 30-cm (diameter) x30-cm (deep) soil cores were transplanted between a hotter, drier location at the base of Rattlesnake Mountain (310 m, 28.5°C air average monthly maximum, 224 mm y^{-1}) and a cooler, moister location near the top of the mountain (844 m, 23.5°C air average monthly maximum, 272 mm y^{-1}). Soils transplanted from the hot, dry, lower site to the cooler and wetter upper site exhibit, after 17 years, almost no respiratory response to temperature (Q10 of 1.1), and have a microbial community structure distinct from non-transplanted soils. These results are at odds with many short-term experiments, suggest a lack of microbial resilience in the lower-site soils even after almost two decades in a changed climate, and cannot be reproduced by current soil models. This study shows that microbial populations responsible for soil heterotrophic respiration may be constrained in surprising ways, with significant consequences for ecosystem-scale carbon cycling.

PNNL's TES research focuses on climate-driven tipping points, specifically microbially-mediated processes destabilizing soil organic carbon. These phenomena are poorly represented in current climate models and are significant sources of uncertainty in predictive models of greenhouse gas flux. Such uncertainty can be reduced only by understanding the fundamental processes underpinning measured fluxes. Resolution of these fundamental biogeochemical processes may be an important bridge between pore-scale reaction models, ecosystem box models, and regional-scale models informing the Community Land Model.

NAME: Chongxuan Liu

ORGANIZATION: Pacific Northwest National Laboratory

PROGRAM AFFILIATION: TES

ABSTRACT TITLE: A Unified Multi-Scale Model for Cross-Scale Assessment of Biogeochemical Process Models in Soils

ABSTRACT: The mathematical representations of soil biogeochemical processes vary with scale. Mechanistic, reaction-based approaches are typically used to describe microbial growth, respiration, organic carbon degradation and CO_2 production at the pore and laboratory scales, while empirical, correlation based approaches are often used at the watershed and regional scales. Soil biogeochemical processes mechanistically occur at the pore-scale that fundamentally control moisture migration, organic carbon degradation, and CO_2 fluxes in soils at the larger scales. The objective of this research is to develop a common modeling approach that can be used to assess the cross-scale manifestation of mechanistic biogeochemical processes. One major challenge for the development of such an approach is that fundamental physical laws governing moisture migration and materials fluxes vary as scale increases from the pore to core, from the core to geological facies, and from the facies to watershed and regional scales. In this presentation, we will report a unified multi-scale model (UMSM), which uses a single set of mathematical equations to simulate moisture migration and materials fluxes at different scales under both saturated and unsaturated conditions. The model unifies physical laws in free water nodes (pores, ponds, lakes, oceans, and rivers) and in porous media nodes (aggregates, aquifer), providing an efficient and cost-effective way to assess the cross-scale manifestation of biogeochemical processes. A series of validation cases were performed to evaluate the modeling approach. The model was then used to describe the pore to core scales of moisture migration in a soil core with its pore structure characterized using computerized x-ray tomography (XCT), and to simulate core to watershed scale of flow and transport with mixed aquifer and surface water bodies. The model is readily to incorporate reaction-based microbial processes in soils. The future work will focus on: 1) development of reaction-based biogeochemical models to describe microbially mediated organic carbon degradation and CO_2/CH_4 production in soils in collaborating with the experimental part of this TES project; and 2) cross-scale evaluation of biogeochemical process models using the UMSM and other modeling approaches such as reaction-based community land model (CLM). The future research will target the soil organic carbon degradation at the Disney Wilderness Preserve (DWP) site, where several TES projects are ongoing at the field scale. The UMSM and reaction-based biogeochemical models will be evaluated at the site.

This research is part of the PNNL/TES project.

NAME: Jerry Melillo
ORGANIZATION: The Ecosystems Center, MBL
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Climate Change and Soil Feedbacks to the Climate System: new process-level insights from a 22-year field study

ABSTRACT: A key question in earth system science is: Will warming lead to increased soil organic matter decay and an accelerated release soil carbon as CO_2? If the answer is yes, a self-reinforcing feedback would result with warming begetting warming. In 1991, we established a replicated, *in situ* soil-warming experiment at the Harvard Forest in central Massachusetts to address this question.

We have measured rates of soil respiration from warmed and control plots monthly from April through November over the entire course of the study. Periodically, we have also made measurements were of fine root respiration. Initially, warmed plots had higher soil respiration than controls, but after about a decade, the warming-accelerated CO_2 production decreased and returned to background levels. However, during the last seven years of the study (years 16-22), soil respiration increased in the warmed plots relative to the controls – a long-term response to soil warming never before documented.

Measurements we have made over the first 15 years of the study showed the depletion of the soil's labile carbon pool and a loss of about 30 percent of the carbon stored in the forest floor in the warmed plots. Based on a variety of measurements made in the warmed and control plots, we hypothesize that much of the carbon respired over the last seven years of the study has come from the recalcitrant soil carbon pool – "the recalcitrant decomposer hypothesis." Measurements supporting this hypothesis include: 1) an increase in oxidative enzyme potential in the warmed plots after two decades of warming; and 2) an increase in microbial carbon-use efficiency (CUE) associated with the degradation of complex (recalcitrant) carbon compounds such as phenol after long-term warming, but no change in the CUE of simple carbon compounds such as glucose[1]. We also have preliminary data showing a shift in microbial community structure in the warmed plots. Currently, we are exploring possible relationships between this microbial community restructuring and any increases in taxa or pathways adapted to recalcitrant carbon decomposition. We are also beginning to refine a microbial-enzyme model to explore the proposition that the soil microbial community will adapt to long-term warming in a way that will lead to a depletion of the recalcitrant soil carbon stocks and a self-reinforcing feedback to the climate system.

[1] Frey, S.D., J. Lee, J.M. Melillo, J. Six. 2013. Soil Carbon Cycling: The temperature response of microbial efficiency and its feedback to climate. *Nature Climate Change.* 3, 395–398 doi:10.1038/nclimate1796.

TERRESTRIAL ECOSYSTEM SCIENCE

UNIVERSITY-LED RESEARCH

NAME: John Bain
ORGANIZATION: Old Dominion University
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Optimizing Ground-Penetrating Radar for Measurement of Coarse Root Dynamics

ABSTRACT: The temporal and spatial quantification of coarse roots has proven to be one of the most difficult aspects of belowground ecology. Coarse roots play a significant role in belowground carbon cycling and will likely play an increasingly crucial role in belowground carbon sequestration as atmospheric CO_2 levels continue to rise. Ground-penetrating radar (GPR) has been shown to be an effective, nondestructive method of quantifying biomass of coarse roots. GPR propagates electromagnetic waves into the soil, reflecting a portion of the energy back to the surface whenever the waves change speed as a result of contacting a buried object. 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. In this study, we are exploring various scanning protocols and thresholds of application for GPR use across a variety of environmental conditions. We will be conducting experiments in the sandy soils of a sand-hill mixed oak community in Southeastern Virginia, USA as well as shrub-scrub and long-leaf pine flatwoods in Florida, USA. Using a 1500 MHz antenna, we have begun testing several scanning protocols involving different scan angles and intervals as well as examining current and potential image processing techniques. We are in the process of establishing correlations between the pixel counts from these different scanning protocols and observed root biomass. The most predictive regression equation will be used at our test site in Southeastern Virginia to measure the effectiveness of GPR in estimating coarse root biomass, in identifying root structures under varying levels of soil moisture and soil composition, in quantifying change in root mass over time, and in determining the effect of root shadowing. These techniques will also be applied to shrub-scrub and longleaf pine flatwoods in Florida in the winter of 2012-2013 as well as to measure legacy effects of raised carbon levels due to an 11-year carbon enrichment experiment at Kennedy Space Center that ended in 2007. This nondestructive method of root quantification could provide a means for rapid and repeatable measurement of belowground structures and as the technique is refined and thresholds are better established, potentially be applied to a wider variety of ecosystems to obtain long-term data on coarse root dynamics.

NAME: Dennis Baldocchi
ORGANIZATION: University of California, Berkeley
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Findings from a decade-plus study of comparative carbon, water and energy fluxes from an oak

ABSTRACT: We have been collecting carbon and water fluxes of an oak savanna and annual grassland in the Mediterranean climate of California since 2000. This long and continuous and comparative data record gives us an unprecedented ability to understand and quantify the interannual variations in carbon, water and energy exchange of contrasting functional types and how they respond to the highly variable annual precipitation inputs.

Our scientific approach uses the eddy covariance to measure the net and gross fluxes of trace gases between ecosystems and the atmosphere. We augment these measurements with a variety of mechanistic studies that examine the physiological and biophysical control on these fluxes. These efforts involve laboratory and field measurements on the exchange of gases from the soil, leaves and plants, like understory eddy flux measurements, pre-dawn water potential, photosynthetic capacity, soil respiration, soil moisture, monitoring the water table and excavation of roots. To upscale our flux measurements we rely on an assortment of remote sensing measurements. These efforts include measuring light transmission through vegetation, monitoring hyperspectral reflectance of the vegetation, time series of canopy photos to monitor phenology and LIDAR surveys of vegetation structure.

Based on data through the 2010 hydrological year we find that net ecosystem exchange, ecosystem photosynthesis and respiration are -101 +/- 67, 1302 +/- 195 and 1193 +/- 161 gC m^{-2} y^{-1}, respectively, for the oak savanna, indicating it is a sink for carbon. In comparison, the annual grassland is carbon neutral; its mean annual sums for net ecosystem exchange, ecosystem photosynthesis and respiration are 19 +/- 109, 814 +/- 251 and 833 +/- 251 gC m^{-2} y^{-1}, respectively.

Together we digest, distill and evaluate this information fluxes and biophysical structure and function of the canopies through a hierarchy of biophysical models, derived from the CANVEG family. Our most recent efforts have been to build on the efforts from our field work to develop two contrasting models. One model, CANOAK-3D, simulates the complex three-dimensional light environment of the savanna to compute photosynthesis and leaf energy balance fluxes. The other model, the Breathing Earth System Simulator--BESS, runs with remote sensing information derived from MODIS to produce flux information on carbon and water exchange at high spatial resolution (1-5 km) across the globe, from days to years. Both models were found to perform well, when compared with data from either the savanna site or the Ameriflux network.

NAME: Holly Barnard
ORGANIZATION: University of Colorado
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Understanding the role of landscape structure in coupled carbon and water dynamics

ABSTRACT: One of the largest knowledge gaps in environmental science is the ability to understand and predict how ecosystems will respond to future climate change. The links between vegetation, hydrology, and climate that control carbon sequestration in biomass and soils remain poorly understood. Topography is known to strongly influence microclimate; yet, investigations using natural gradients associated with topography have yielded equivocal conclusions concerning the environmental controls of carbon dynamics. Our study examines how tree response to drought varies between species and across topography in a montane headwater catchment. Foliar $\delta^{13}C$ was compared between a wet and dry year to characterize changes in water use efficiency (WUE) in the area's two dominant tree species: ponderosa and lodgepole pine. Lodgepole pine had a significant increase in $\delta^{13}C$ in the dry year, whereas, ponderosa pine did not significantly change from the wet to dry year. Topographically-derived GIS surfaces for incoming solar radiation and topographic wetness index were used to model spatial variability in drought response. Improved spatial models may better predict topographical influence on drought sensitivity. The stark contrast in the WUE response of ponderosa and lodgepole pine highlights the importance of understanding variation at the individual catchment scale to effectively model and predict regional and global tree response to drought and shifts in species range under changing future climate conditions.

NAME: Scott Bridgham
ORGANIZATION: University of Oregon
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Response of soil efflux to experimental warming and precipitation intensity depends upon latitudinal climate gradient in Pacific Northwest grasslands

ABSTRACT: Soil respiration is expected to increase as global temperatures rise, amplifying climate forcing. Most studies have been conducted at single sites, making it difficult to generalize results. Additionally, acclimation to warming has been observed repeatedly in experimental studies, although the mechanism remains unclear and this response does not occur in Earth system models. To deconvolve local versus regional climatic controls, we examined soil respiration along a 520-km latitudinal climate gradient in three Pacific Northwest grasslands, with increasingly Mediterranean-like climates from north to south. Beginning Fall 2010, we implemented a fully-factorial treatment combination of 2.5-3^{o}C warming and 20% added precipitation intensity at each site. We are also sampling labile soil carbon pools seasonally to determine if there is a relationship with any observed acclimation response. The response of soil respiration varied seasonally among sites, consistent with soil temperature and moisture trends imposed by the regional climate gradient. Soil respiration was highest in the wettest/warmest conditions (Spring), lower in cool/wet conditions (Fall and Winter), and lowest when dry (Summer). The gradient also influenced seasonal transition rates, with the switch between a stimulatory to an inhibitory effect of experimental warming moving progressively later in the spring from the southern to the northern site due to accelerated moisture limitation. Precipitation stimulated respiration in the most southern site during May and July, consistent with respiration being primarily moisture limited. Treatment effects diminished after July 2011, which may indicate soil acclimation although there is no evidence to date of decreased labile soil carbon. Seasonal shifts in the primary physical limitations on respiration varied predictably along the climate gradient, emphasizing the importance of regional responses to climate change within an ecosystem type. Potentially most importantly, our results indicate that soil respiration may be minimally responsive to warmer temperatures during periods of drought, which may become more pervasive in many ecosystems in the future.

NAME: Scott Bridgham
ORGANIZATION: University of Oregon
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Pushing the limit: experimental evidence of climate effects on plant range distributions

ABSTRACT: There is increasing evidence that climate change is leading to shifts in plant species' geographic ranges. It is projected that many species will need to establish viable populations beyond their current ranges or risk extinction in coming decades. Recently observed range shifts offer strong empirical evidence of climate change impacts, but it is impossible to decouple climate effects from those of other environmental changes. Because many factors at both local and regional scales control species' range-limits, experimentation is essential to test the underlying mechanisms. To this end, the main objective of this project is to determine how climate change will affect the distribution of native plants in Pacific Northwest (PNW) prairies. We embedded a fully factorial manipulation of temperature (+2.5-3.0°C) and wet-season precipitation intensity (+20% above ambient) into a 520-km latitudinal climate gradient in three upland prairies in the PNW, with increasingly severe Mediterranean climate conditions from north to south. Treatments were initiated in 2010, and in the fall of 2010 and 2011, twelve native forbs and grasses that have their northern range limits within the PNW were seeded into each plot. Germination, survivorship, plant size, and seed set were measured in 2011 and 2012.

For species' planted within their current range, increased temperature negatively impacted recruitment, but this negative heating effect disappeared when the species were moved poleward beyond their current range. Germination presented the most significant hurdle to species' success. Once species were able to germinate, a species' current range no longer impacted survivorship, plant growth, or fecundity. Instead, warming negatively impacted survivorship regardless of current range, but if individuals were able to survive, they grew bigger and produced more seeds in the heated treatments. Decreased survivorship in warmed plots was in part mediated by an increase in competition in these plots (determined by a competition removal experiment), and increased plant growth in the heated treatments could be explained by an indirect effect of increased nutrient availability. We found minimal effects of added precipitation on any life-history stages, but when significant, increased precipitation decreased germination and survivorship. Our two years of results are consistent with predictions that many species will need to expand their ranges poleward or higher in elevation to successfully maintain viable populations. However, multiple years of data will be necessary to understand if, once established, these species' will be able to maintain positive population growth. Our results demonstrate the importance of using regional-scale climate manipulations and the need for longer term experimental studies on the demographic responses that control species' distributions.

NAME: Scott Bridgham
ORGANIZATION: University of Oregon
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Consistent shifts in community composition and diversity in response to experimental climate manipulations across a latitudinal gradient in Pacific Northwest prairies

ABSTRACT: Projected changes in climate are expected to have widespread effects on plant community composition and diversity in the coming decades. However, multi-site, multi-factor climate manipulation studies are rare to examine whether observed responses are regionally consistent and whether multiple climate perturbations are interdependent. To investigate climate effects on plant community composition, we implemented a fully factorial climate manipulation of warming (+2.5-3°C) and increased wet-season precipitation (+20%) at three sites across a 520-km latitudinal gradient from southern Oregon to central Washington. All sites were seeded with a nearly identical mix of native grasses and forbs in the fall of 2009 and climate treatments were initiated in 2010. Plant cover was measured in each plot for three consecutive years to address our three hypotheses: (1) under a warmer climate, plant diversity and richness would decrease across sites, but increased precipitation would offset these effects by ameliorating water stress; (2) warming would favor introduced species; and (3) community composition of warmed plots would become more similar to their ambient temperature counterparts in sites further south, but added precipitation would reduce such trends by alleviating drought stress.

Warming altered plant community composition (including functional composition), decreased diversity, and increased total cover with warmed Northern communities becoming more like those found further south over time. In particular, after two full years of warming, annual and introduced cover increased suggesting that the observed biogeographic pattern of plant functional groups in West Coast prairies of the US (invasive annual plant communities in CA and southern OR, perennial plant communities from central OR north) is at least in part due to the direct effects of climate. Additional precipitation during the rainy months did little to alleviate drought stress, and had minimal effects on community structure. Our results suggest that with the increase in drought severity projected for the region, prairies of the Pacific Northwest may face an increase of invasion by annuals, similar to what has been observed in California, resulting in novel species assemblages and shifts in functional composition, which in turn may alter ecosystem functions.

NAME: Zoe Cardon
ORGANIZATION: Ecosystems Center, MBL, Woods Hole, MA
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Hydraulic redistribution of water through plant roots – implications for carbon cycling and energy flux at multiple scales

ABSTRACT: The rhizosphere (the volume of soil around plant roots, influenced physically and/or chemically by those roots) is a fundamental commodities exchange in terrestrial ecosystems. Carbon moves from roots to the microbial community, and the microbial community uses readily-available carbon for energy and to build biomass, influencing soil CO_2 flux and availability of nutrients to plants in the process. In the rhizosphere, interacting carbon and nutrient cycles are strongly affected by fluctuating soil water content driven by plant transpiration and hydraulic redistribution (HR) of soil water through root systems. During HR, soil water flows from wet soil zones into roots, through the root system, and out of roots into dry rhizosphere soil, exactly where the carbon and nutrient commodities exchange is active. Though warming-induced increases in atmospheric demand for evaporation, and resulting soil drought, are expected in the future, the current generation of dynamic vegetation and earth system models do not include HR. We are examining how HR affects soil carbon and nutrient cycling, as well as transpiration, plant carbon gain, and energy fluxes, in seasonally dry ecosystems. We are combining greenhouse work with Ameriflux site data, small-scale mechanistic and large-scale ecosystems and earth system modeling to explore the interactions shown in Fig. 1, particularly focusing on upward HR ("hydraulic lift", HL) that occurs in seasonally dry systems during drought. HL provides a mechanism for simultaneously ameliorating limitations in shallow soil water content and plant nutrient availability, potentially enhancing plant carbon gain through "direct" and "indirect" pathways shown of Fig. 1, while also stimulating heterotrophic respiration. Whether net ecosystem exchange will shift positive or negative as a function of HR will depend on the relative strengths of direct and indirect effects mediated by plants and microbes, the signs and strengths of their component processes, the intensity of future drought, and the time scale over which HR's effects are considered.

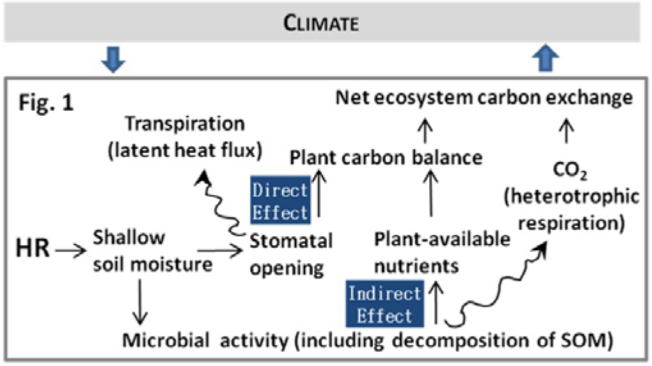


Fig. 1

<u>RESULTS TO DATE</u>: We have established a greenhouse experiment that will hold availability of water to plants constant, while simultaneously preventing or allowing HL by controlling the timing of deep watering. Microbial, soil, and plant response will be assessed. We have also developed a new strategy for genetically engineering bacteria to use as microbiosensors to get the "microbial point of view" of dynamic water availability around plant roots. Root-scale reactive transport and microbial modeling using MIN3P will be informed by greenhouse and microbiosensor data, and will inform selection of key processes to be included during modification of larger scale models. We have gathered Ameriflux eddy flux and soil moisture data from most of our target sites, begun exploring the data for potential signatures of HL during dry seasons, and begun site-specific modeling capturing major drivers of water, energy, and carbon exchange (CLM4.0). Finally we

have tested configurations (and domain boundaries) for the regional climate model RegCM4-CLM4 and identified the configuration with best performance in the North American domain.

NAME: Jeff Chanton
ORGANIZATION: Florida State University
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Identifying Dissolved Organic Matter Decomposition in Northern Peatlands using Complimentary Analytical Techniques

ABSTRACT: We determined the composition and reactivity of DOM from representative bog and fen sites in the Glacial Lake Agassiz Peatlands (GLAP) in northern Minnesota, USA. We applied four complementary techniques: electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR MS), proton nuclear magnetic resonance spectroscopy (^{1}H-NMR), specific UV absorbance (SUVA) and excitation-emission matrix (EEM) fluorescence spectroscopy. We observed that the vast majority (> 80%) of molecular formulas that appear in the surface bog DOM are also present at 3 m depth, indicating that DOM in the bog is largely refractory. In contrast to bog samples, a considerable number of new compounds with low O/C and high H/C elemental ratios were observed in the 3 m fen horizon relative to surface samples. These results indicate a more pronounced difference in the composition of surface and deep DOM in the fen.

SUVA, determined at 254 nm, was strongly correlated with lower aromaticity in deep fen samples relative to deep bog samples. This trend was verified by ^{1}H-NMR. Aromatic and carbohydrate components represented up to 70% of deep bog DOM but comprised a much smaller proportion of deep fen DOM, which was dominated by functionalized and non-functionalized aliphatics. Molecular formula data determined by FT-ICR mass spectrometry were consistent with results from optical and NMR spectroscopy measurements and showed that compounds with low O/C and high H/C were generated with depth in the fen. Such compounds were absent in both surface fen and in surface and deep bog samples respectively, providing further evidence of qualitative and quantitative differences in the evolution of DOM in fens and bogs. These differences, attributed to either variations in source vegetation or environmental factors that render DOM more reactive in fen sites and less reactive in bog sites, have important implications for the response of peatlands to climate change, since climatic change leading to moister conditions may enhance the abundance of sedge-dominated fens and increase the pool of more labile soil carbon.

NAME: William Cooper
ORGANIZATION: Florida State University
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Linking Chemical Signatures and Microbial Communities that Affect Carbon Cycling in Northern Peatlands

ABSTRACT: Global peatlands sequester half as much carbon as that contained in the atmosphere. However, the response of these large carbon reservoirs to global warming remains uncertain. In this presentation the results of experiments designed to identify the reactive and refractory dissolved organic matter (DOM) pools and the composition of solid phase peat in a bog habitat within peatlands in the Marcell Experimental Forest, northern Minnesota, will be described, along with accompanying differences in microbial communities. These experiments included advanced analytical techniques[1] (ultrahigh resolution (UHR) mass spectrometry, PARAFAC modeled 3-D excitation-emission matrix [EEM] fluorescence spectroscopy), ^{13}C and ^{31}P NMR, FT IR spectroscopy and a combination of next generation sequencing and metagenomics.[2] Surface peat (0-10 cm) was characterized by high carbohydrate concentrations, high C/N , and relatively low aromaticity . Concentrations of organic P in the solid phase were relatively small and were dominated by orthophosphate monoesters (25–35 mg P kg^{-}1 soil), with smaller concentrations of orthophosphate diesters (5–7 mg P kg^{-1} soil). Surface DOM was characterized by high DOC concentrations, low aromaticity and abundance of amino-sugars and proteins derived from plant materials. In more decomposed layers at 30-50 cm depth, UHR mass spectra identified distinctly different reactive and refractory DOM pools, as well as the appearance of lipid-like compounds of apparent microbial origin both in the solid phase peat and DOM. PARAFAC modeled EEM revealed fluorescent components (products and reactants) that were consistent with microbial processing. An increase in the amount of phosphonates was observed at this depth and was coincident with a decrease in orthophosphate. This shift was accompanied by an increase in the organic nitrogen both in the solid and aquous phases. Below 75 cm, slower degradation of organic matter under anaerobic conditions and stable enzymatic activity was observed, along with an increase in the degree of humification of both the solid and aqueous phases that was reflected by an increase in the amount of condensed hydrocarbons. Inorganic phosphorus (orthophosphate) becomes the most abundant form of phosphorus below 75cm, suggesting a surprising reactivity or organic-P. Microbial community structure corresponded strongly to the vertical stratification of dissolved organic matter (DOM) and solid phase quantity and composition. Taken together, the microbial, chemical and spectroscopic analyses of different peat bog profiles have identified three distinct zones within the peat formation that have unique properties. Quantity and quality of DOM, solid phase peat and surface vegetation were significant variables governing microbial community turnover spatially and seasonally.

NAME: Peter Curtis
ORGANIZATION: The Ohio State University
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Resolving scale-dependencies in the effects of canopy structure on carbon, water, and energy fluxes in a mixed deciduous forest.

ABSTRACT: The future of the North American carbon stocks and fluxes remains uncertain as mixed deciduous forest of the Midwest and East U.S. transition from early to middle and late successional stages. As the succession happens, the canopy structural and functional attributes change which affect a multitude of phenomena, ranging from canopy light, water and nutrient usage to turbulent mixing of air within the canopy. By taking advantage of the Forest Accelerated Succession ExperimenT (FASET), in which aspen and birch were girdled in an area of 39 ha, we intend to improve the current understanding of how carbon and water vapor fluxes respond to changes in the canopy structure as the vegetation recovers from the imposed disturbance.

Our ongoing study is a multi-front approach, where computer models operating in a wide range of scales (from individual trees to regions) aid the interpretation of empirical measurements of the response of water, carbon, and energy fluxes to the imposed structure/function changes. These include OLAM – a new global-regional model with extreme zoom-in capabilities, RAFLES – a high-resolution canopy resolving large eddy simulation and tRIBS+VEGGIE – a high resolution vegetation resolving hydrological model. We find strong scale dependencies for the effects of structural changes, and that physiological processes, such as tree-level hydrodynamics and nutrient cycling, are critical to the prediction of stomata conductance and carbon dynamics. Our models were able to predict some of the outcomes of structural changes to NEE and forest carbon storage by resolving these functional processes at very high resolutions. Our results can reduce the uncertainty of forecasts of terrestrial carbon storage and advance the formulation of forest management guidelines for enhancing carbon sequestration in older forests and in forests experiencing moderate disturbance.

NAME: Jean-Christophe Domec
ORGANIZATION: North Carolina State University
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Convergence of the effect of root hydraulic functioning and root hydraulic redistribution on ecosystem carbon balance and drought-induced vegetation mortality across divergent forest ecosystems

ABSTRACT: Deep root water uptake and hydraulic redistribution (HR) play a major role in forest ecosystems during drought, but little is known about the impact of climate change on root-zone processes influencing HR and its consequences on drought-induced mortality and on carbon fluxes. Using data from three old growth sites in the western USA, three mature sites in the eastern USA, one site in southern Brazil, and simulations with the process-based model MuSICA, our objectives were to show that HR can 1) mitigate the effects of soil drying on root functioning, 2) reduce tree mortality, and 2) have important implications for carbon uptake and net ecosystem exchange (NEE). In a dry, old-growth ponderosa pine (USA) and a eucalyptus stand (Brazil) both characterized by deep sandy soils, HR limited the decline in root hydraulic failure and tree mortality and increased dry season tree transpiration (*T*) by up to 30%, which impacted NEE through major increases in gross primary productivity (GPP). The presence of deep-rooted trees did not necessarily imply high rates of HR unless soil texture allowed large water potential gradients to occur, as was the case in the wet old-growth Douglas-fir/mixed conifer stand. At the Duke mixed hardwood forest and at the New Mexico piñon /juniper site characterized shallow soils, modeled HR was low but not negligible, representing annually up to 10% of *T.* At this site, in the absence of HR, it was predicted that annual GPP would have been diminished by 7-19%. At the coastal loblolly pine plantation, characterized by deep organic soil, HR limited the decline in root conductivity by more than 50%, prevented tree mortality and increased dry season *T* by up to 40%. Under future climate conditions (elevated atmospheric [CO_2] and temperature), HR is predicted to be reduced by up to 45-50%; reducing the resilience of trees to droughts and increasing mortality. We concluded that the predicted reductions in HR under future climate conditions are expected to play an important regulatory role in land–atmosphere interactions by affecting tree death, whole ecosystem carbon and water balance. We suggest that root distribution should be treated dynamically in response to climate change and that HR and its interactions with rooting depth and soil texture should be implemented in soil–vegetation–atmosphere transfer models.

Keywords: root cavitation, carbon sequestration, drought-induced root failure, hydraulic redistribution, MuSICA Model, night transpiration, root conductivity, soil water content

NAME: James Ehleringer
ORGANIZATION: University of Utah
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Evaluation of the seasonal dynamics of photosynthesis and drought stress in CMIP5 models

ABSTRACT: In many northern terrestrial ecosystems, photosynthesis during summer is fueled by the accumulation of snow and soil moisture during winter and spring. With longer growing seasons expected during the next several decades as a consequence of climate warming, increasing drought stress is possible if earlier onset of photosynthesis and transpiration is not balanced by increases in precipitation during the growing season or increases in ecosystem water use efficiency (WUE). We present long-term carbon isotope records in atmospheric CO_2 and tree ring cellulose at two AmeriFlux sites (Wind River and Metolius) as examples to illustrate how ecosystem WUE may respond to seasonal and interannual variations in soil water conditions. Here we examined the timing of spring photosynthetic onset in CMIP5 models using eddy covariance observations and atmospheric CO_2 mole fraction observations. Our results indicate that many of the CMIP5 models exhibit an early onset bias in photosynthesis and transpiration for the contemporary period. In some models, the early onset of photosynthesis appears to cause ecosystems to more rapidly consume soil moisture reserves, leading to low biases in latent heat fluxes during mid-summer, and as a consequence, greater atmospheric heating and reduced precipitation over the interior of northern continents. We also discuss how photosynthesis and drought stress are likely to change during the 21st century and how contemporary biases may influence future projections of change. We provide a new set of physiological mechanisms that may reduce spring photosynthesis biases in climate models.

NAME: David Genereux
ORGANIZATION: North Carolina State University
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Investigating the balance between uptake and export for inorganic carbon discharged to rainforest streams from regional groundwater, Costa Rica

ABSTRACT: Recent water and carbon data from the lowland rainforest at La Selva Biological Station in Costa Rica suggest that old regional groundwater elevated in dissolved inorganic carbon (DIC) flows beneath watershed topographic boundaries and discharges upward into streams and riparian wetlands, strongly influencing concentrations and fluxes of both DIC and dissolved organic carbon (DOC) and potentially augmenting CO_2 fluxes from streams and wetlands. This suggests accurate understanding of the carbon cycle and source/sink status of the ecosystem from field data requires accounting for carbon inputs from regional groundwater.

One objective is to determine the extent to which old DIC discharged to streams by regional groundwater is incorporated into the modern biological carbon cycle in the study streams. In other words, for this DIC, what is the balance between export from the site (via stream discharge, or degassing from streams) and uptake via in-stream photosynthesis? The latter could be seen as a short-term sequestration of old DIC from regional groundwater in the riparian corridor of the rainforest watersheds. We are evaluating this export-uptake balance by measuring particulate organic carbon (POC) concentrations and stable isotope values ($\delta^{13}C$), as well as atomic C:N ratios. *We hypothesized that if DIC from regional groundwater is being fixed via in-stream photosynthesis, then the POC of the streams will reflect that isotopically-distinct DIC source.*

Our focus includes two adjacent streams: the Arboleda that receives significant regional groundwater (40-50% of stream discharge), and the Taconazo that receives none. The POC concentrations were 0.16 to 1.59 mg C L^{-1} in the Arboleda and 0.50 to 3.27 mg C L^{-1} in the Taconazo; trends in concentration appear linked to stream flow in each system. The two streams had very different $\delta^{13}C$-DIC values due to the influence of regional groundwater in the Arboleda (-4.4‰ in the Arboleda, -22.4‰ in the Taconazo). Given the contrast in $\delta^{13}C$-DIC, and with most primary producers in the streams likely being C3 algae (carbon isotope fractionation of about -20‰ upon uptake), domination of stream POC by in-stream primary production would likely lead to very different $\delta^{13}C$-POC values for the streams: about -42‰ in the Taconazo and -24.4‰ in the Arboleda. But, this was not observed. The $\delta^{13}C$-POC distributions were very similar for both streams and fell within a range of -39 to -22‰. The median $\delta^{13}C$-POC for the Arboleda was -26.7‰ and the median C:N ratio was 16.7; corresponding values for the Taconazo were -27.1‰ and 15. For the POC in both streams, C:N ratio and $\delta^{13}C$ fell within the range typical of soil organic matter dominated by terrestrial C3 vegetation.

These results strongly suggest that old DIC from regional groundwater is not significantly incorporated into the modern biological carbon cycle in the Arboleda stream, likely due to light limitation on rates of photosynthesis in the streams beneath the rainforest canopy. The implication is that large DIC inputs to surface water from regional groundwater are exported from the rainforest with stream discharge or degassed as CO_2 (i.e., this DIC experiences minimal within-watershed sequestration, and thus is necessarily augmenting carbon fluxes across the air-water interface and out of the watershed with stream flow). Further work is underway using stable isotopes to determine if the DIC signal from regional groundwater is present in rainforest DOC. Based on the POC results, we hypothesize that such a contribution is low.

NAME: Jeff Hatten
ORGANIZATION: Oregon State University
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Exploratory Research - Volatile organic compounds as indicators of belowground processes: Partitioning heterotrophic and autotrophic forest soil respiration

ABSTRACT: Research on soil respiration is complicated by the fact that CO2 is an end member which carries very little information about its source (isotopic-only). Therefore, partitioning soil respiration into autotrophic and heterotrophic sources often requires methods that are destructive, invasive, and/or expensive. In this study we have proposed to investigate a new method using the flux of volatile organic compounds (VOCs) from the soil as indicators of CO2 source and below ground processes to non-invasively disentangle this multisource signal.

We hypothesize that the composition and quantity of soil VOCs can be used to separate the respiration associated with roots (autotrophic respiration) and soil organic matter mineralization (heterotrophic respiration). We further contend that the contribution of each autotrophic component, including root respiration, microbial mineralization of root litter, and microbial mineralization of root exudates, can be determined using this approach. We have initiated a greenhouse study of soil respiration and VOC efflux where each respiration component is isolated utilizing pots with and without plants, killed plants, and destructive sampling. The impact of tree species, diurnal cycles, and soil moisture regime will be assessed within the boundaries of this greenhouse study. The objectives of the project are to: 1) Determine the VOCs that uniquely indicate each component of soil respiration; 2) Test the effectiveness of this method over a range of soil moisture conditions; 3) Determine if diurnal cycles affect soil respiration and soil VOC efflux; and 4) Determine if VOCs can uniquely indicate below ground root production of biomass. We will show preliminary relationships of the VOC fingerprint and the experimental manipulations of autotrophic and heterotrophic respiration.

NAME: Ross Hinkle
ORGANIZATION: University of Central Florida
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Carbon Dynamics of the Greater Everglades Watershed and Implications of Climate Change

ABSTRACT: Our newly funded project is focused upon four main objectives, 1) quantification of above- and belowground carbon stocks of terrestrial ecosystems along a hydrologic gradient in the headwater region of the Greater Everglades watershed, 2) development of budgets of ecosystem gaseous carbon exchange (CO_2 and CH_4) across the hydrologic gradient, 3) assessment of the impact of climate drivers on ecosystem carbon exchange, and 4) parameterization of climate-driven terrestrial ecosystem carbon models to estimate regional carbon cycling and examine the potential influence of projected future climate change. A multidisciplinary array of ecological, hydrological and geophysical sampling techniques at multiple spatial scales of measurement is being implemented, including eddy covariance (H_2O/CO_2 and CH_4), closed chamber gas exchange, passive experimental warming and drying, ground penetrating radar (GPR), vegetation and biomass assessment, root productivity and turnover, and soil decomposition assays.

Our network of study sites consists of three ecosystems with contrasting hydrologies: 1) a pine flatwoods site at the Disney Wilderness Preserve (DWP), 2) a seasonal depression marsh at DWP and 3) a sawgrass marsh at the Blue Cypress Preserve. During this first year of the project (and as part of ongoing work), the pine flatwoods has been well characterized for aboveground biomass, litter, and ground cover, and preliminary root cores have been taken to estimate belowground biomass and carbon content of the soil. Ongoing carbon flux measurements have shown this ecosystem to serve as a net C sink even with a prescribed fire event, with annual net ecosystem productivity (NEP) ranging from 237-508 g C m^{-2}. Continuing carbon flux measurements in a saw grass marsh site at the Blue Cypress Preserve also indicate a strong carbon sink with NEP ranging from 180-710 g C m^{-2}.

Ground penetrating radar (GPR) surveys have been initiated in order to map belowground carbon stocks. A method for detecting underground roots has been tested at the pine flatwoods site and a set of preliminary GPR profiles were also collected at the sawgrass marsh site in order to test the ability of GPR to detect changes in peat thickness at large field scales (~100-1000 meters). Chamber-based measurements of gas exchange will commence shortly in order to characterize heterogeneity of carbon fluxes and partition the net exchange amongst above- and below-ground components.

Regional implications of climate change will be investigated through deployment of open top chambers to warm and dry plants and soil at each eddy covariance site. As well, a preliminary carbon dynamics and sequestration model, based upon the G'DAY model has been developed and will be parameterized using data from the towers, chamber measurements, GPR, as well as soil and vegetation samples. The suite of measurement and modeling techniques in place at our central Florida sites will yield a much greater understanding of carbon cycling in the upper-Everglades watershed and Florida as a whole.

NAME: Erik Hobbie
ORGANIZATION: University of New Hampshire
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Fungal functioning in a pine forest: evidence from a 15N-labeled and 13C-labeled global change experiment

ABSTRACT: We used natural and tracer carbon and nitrogen isotopes in a *Pinus taeda* Free Air CO_2 Enrichment experiment at the Duke Forest to investigate the functioning of ectomycorrhizal and saprotrophic fungi in carbon and nitrogen cycling over a six-year period. CO_2 enrichment (+200 ppm; resulting CO_2 decreased in $\delta^{13}C$ by 12‰) began in 1996 and a ^{15}N tracer was applied in 2003. Fungi were sampled in 2004 (natural abundance and tracer) and 2010 (just tracer) and $\delta^{15}N$ and $\delta^{13}C$ patterns compared against other ecosystem pools.

Ectomycorrhizal fungi with hydrophobic ectomycorrhizae (e.g., *Cortinarius*) acquired nitrogen from the Oea horizon whereas taxa with hydrophilic ectomycorrhizae (e.g., *Russula* and *Lactarius*) acquired nitrogen from the Oi horizon. ^{15}N enrichment for *Cortinarius* and *Amanita* did not correspond to any measured bulk pool, suggesting that persistent pools of organic nitrogen supplied these two taxa. Saprotrophic fungi included those colonizing pine cones (*Baeospora*), wood, litter, and soil (*Ramariopsis*), with both $\delta^{15}N$ and $\delta^{13}C$ of taxa reflecting these source preferences. Fungal ^{15}N enrichments relative to source nitrogen ranged from 4-9‰; these enrichments were linked in analytical equations to both increased allocation by fungi to hyphal development and decreased nitrogen transfer to host plants. The $\delta^{13}C$ of ectomycorrhizal genera in ambient and elevated CO_2 plots correlated with a slope (4.3±1.2) greater than one, suggesting that these fungi assimilated carbon from two isotopically distinct sources, recent photosynthate and a second and smaller source derived from litter or soil. *Inocybe* and *Cortinarius* incorporated some soil-derived carbon whereas *Lactarius* and *Russula* incorporated some litter-derived carbon. Natural abundance and tracer isotopic labels proved useful for tracking nitrogen and carbon from different sources into fungal taxa and provided new insights into interpreting natural abundance patterns of both $\delta^{15}N$ and $\delta^{13}C$.

NAME: David Hollinger
ORGANIZATION: USDA Forest Service
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Supporting carbon cycle and earth systems modeling with measurements and analysis from the Howland AmeriFlux Site.

ABSTRACT: The overall goal of the proposed work is to understand the various (and interacting) impacts of a changing climate on carbon cycling at the Howland AmeriFlux site, representative of an important component of the North American boreal forest. *Our focus is on quantitatively and continuously partitioning respiration to better constrain carbon cycle models.* Specifically our goals include (1) using manipulative and isotopic methods to partition soil respiration into heterotrophic and autotrophic components, (2) evaluating whether a long-term trend of increasing C sequestration is related to reduced respiration or enhanced primary productivity, (3) determining what observational data best reduce uncertainties in simulated respiratory fluxes and below-ground processes, and (4) investigating the relationships between CO_2 and CH_4 emissions in this mosaic landscape of moderately well drained and very poorly drained soils.

Six soil respiration chambers have measured soil CO_2 and CH_4 fluxes, soil moisture and temperature at 90 minute intervals since 2011. In September 2012, trenches were excavated to 50cm depth around three of the chambers. Plastic tarp was placed along the trenched walls to prevent root regrowth into plots and the trenches were backfilled. Following trenching, CO_2 effluxes declined in the trenched plots relative to the control plots, however there was little change in measured CH_4 fluxes between control and trenched following trenching. The change in respiration is a direct indication of autotroph respiration.

Eddy flux measurements of whole ecosystem net carbon exchange indicate that this mature conifer forest has continued to sequester carbon (averaging ~ 200 g C m^{-2} y^{-1} since 1996; >300 g C m^{-2} in 2012) and that the rate of C uptake has increased by ~7 g C yr^{-1} ($P<0.01$) since measurements commenced. Much of this increase in C uptake is associated with an earlier start to the growing season in recent years. Whole ecosystem CH_4 flux measurements at Howland supported by TES are described in the companion poster by Shoemaker et al.

Continuous □^{13}C measurements of stem and soil respiration suggest that carbon isotope discrimination differences between the dominant species at the site (red spruce and eastern hemlock) are greater than between autotrophic and heterotrophic sources. This means that the isotopic measurements may not be useful in partitioning respiratory fluxes. However, these data provide important insight into plant water use efficiency and can constrain stomatal conductance parameters in ecosystem models.

NAME: Gabriel Katul
ORGANIZATION: Duke University
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Constraining the simultaneous effects of elevated atmospheric CO2, temperature, and shifts in rainfall patterns on ecosystem carbon fluxes using multi-scale resource optimization theories

ABSTRACT: Increases in atmospheric carbon dioxide concentrations (c_a) will lead to changes in the climate that alters 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 this feedback, the primary pathways by which elevated c_a, T_a, and changing P patterns simultaneously impact ecosystem photosynthesis and respiration must be quantified. This work will 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 initial work (year 1) on using an optimization modeling approach to capture leaf-level stomatal responses to elevated c_a, changes in T_a, vapor pressure deficit and leaf water potential was presented using a meta-analysis on published data sets spanning many climatic conditions and species types.

Our current work (year 2) is focused on bridging the leaf-level processes completed and presented in year 1 to the soil-root system, thereby providing a mathematically usable form for coarse-scale models. Manuscripts dealing with (i) soil and plant hydraulics constraining ecosystem productivity, (ii) physical limits to water transport and carbon uptake, (iii) the interplay between more negative xylem water potentials providing a larger driving force for water transport but also causing cavitation that limits hydraulic conductivity, (iv) modeling interfacial fluxes between the roots and the soil have all been published within the context of optimality formulations or hypotheses.

Over the course of the coming year, the other components of this project will be considered, including modeling of autotrophic and heterotrophic respiratory processes. Autotrophic processes reflect changes in biomass pools determined using standard biomass budget equations, which are being modified to include carbon allocation rules derived from resource optimization theories that explicitly consider soil and foliage nutrition. For heterotrophic processes, three interacting soil carbon pools must be considered at minimum: litter, more stabilized SOM, and microbial biomass. Rates of decomposition, nitrogen mineralization, nitrification, and de-nitrification are being modeled together with soil moisture and temperature. Our final goal is to use a novel dimension reduction approach to simplify the multi-dimensional phase-space of this detailed model to a system of a few ordinary differential equations and prepare this simplified model for incorporation into existing climate-carbon models.

NAME: Gabriel Katul
ORGANIZATION: Duke University
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: The role of stomatal signaling on plant water and carbon balance

ABSTRACT: Stomata respond to environmental stimuli through physical and biochemical signaling mechanisms that regulate ecosystem water and carbon fluxes. In particular, species have been observed to fall along a spectrum of stomatal sensitivity to drought. At one end of this spectrum, stomata close rapidly under drought conditions such that leaf water potential is regulated within a narrow range and xylem cavitation is limited, but carbon uptake is reduced (i.e. isohydric behavior). At the other end, stomata remain open during drought, which promotes carbon uptake at the expense of decreased leaf water potential and extensive xylem cavitation (i.e. anisohydric behavior). One hypothesis suggests that these strategies emerge from a combination of a biochemical signal indicating drying soil and a physical signal indicating drying of the canopy or upstream xylem. In this framework, isohydric plants are more sensitive to the soil signal.

A simplified model for the soil-plant-atmosphere system that incorporates these two signaling mechanisms is proposed to delineate their relative importance in water and carbon fluxes. In a first-order analysis, it is assumed that stomatal conductance and canopy gas exchange respond to soil moisture, a slowly varying external environmental state, and plant water potential, a rapidly varying internal state. The relative strengths of these two feedback mechanisms lead to a range of dynamics in the coupled soil-plant system consistent with the spectrum of stomatal control strategies and the trade-off between gas exchange and hydraulic safety. These preliminary model results suggest soil moisture feedback is an efficient mechanism for controlling plant water potential and xylem cavitation. Further, we deduce relations between soil, climate, and stomatal control that can be linked to the geographic distribution of these stomatal control strategies thereby allowing, for the first time, the spectrum of stomatal control strategies to be incorporated into large-scale land-surface modeling schemes.

NAME: Ralph Keeling
ORGANIZATION: Scripps Institution of Oceanography
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Large-scale shifts in land metabolic activity indicated by changing seasonal cycle of atmospheric CO_2

ABSTRACT: PROJECT OBJECTIVES: This proposal has the overall goal of producing datasets relevant for documenting changes in the global carbon cycle and improving understanding of how land ecosystems may influence and be influenced by future CO_2 changes 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 CO_2) on northern extra-tropical ecosystems over multi-decadal time scales, using records extended over the past 50 years. Targets for model improvement include improved depiction of the response of northern extra-tropical ecosystems

RESULTS: Observations of atmospheric CO_2 concentration at ground-based sites in the Northern Hemisphere show increasing trends in seasonal amplitude over the last few decades, with the largest changes at high northern latitudes. But the long-term change in CO_2 amplitude, and especially its spatial pattern, cannot be well-characterized using existing datasets because only Mauna Loa, Hawaii (MLO, 20°N) and Barrow, Alaska (BRW, 71°N) have records extending back to the 1950s-60s. At both of these sites, the timing of CO_2 drawdown has advanced by roughly one week, but the trends in amplitude differ: the amplitude at Mauna Loa increased by 15±5 % over the past 50 years while the amplitude at Barrow increased by at least twice as much.

Further insight into the amplitude changes is now possible by comparing CO_2 data from a recent large-scale aircraft campaign (the HIAPER Pole-to-Pole Observations or HIPPO) with observations made 50 years earlier during the International Geophysical Year (IGY). The comparison reveals, with unprecedented clarity, the magnitude and spatial pattern in long-term CO_2 amplitude trends and resolves a strikingly large (~50%) amplitude increase north of 45°N. The increase evidently requires an increase in summer-time NPP of order 50% focused on boreal forests, which is very difficult to explain unless major structural changes have occurred in the boreal forests the 50-year period. The trends south of 45°N are considerably smaller. The overall pattern with latitude is therefore consistent with the ground-based time series from Mauna Loa and Barrow. The Mauna Loa amplitude shows large quasi-decadal variability, which correlate 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. The overall rise at Mauna Loa is not explained, however, by the PDO. The pattern revealed by the airborne and ground-based data may require both large long-term increases in NPP north of 45°N, and also small reductions in the seasonal CO_2 exchange at lower latitudes.

NAME: Joel Kostka
ORGANIZATION: Georgia Institute of Technology
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Toward a predictive understanding of microbial carbon turnover in a northern peatland.

ABSTRACT: Global peatlands sequester one-third of all soil carbon and currently act as major sinks of atmospheric CO_2. The goal of this project is to investigate changes in the lability of soil organic matter and the composition of decomposer microbial communities in response to the climatic forcing of environmental processes that determine carbon storage and sequestration in peatlands. A combination of cutting-edge analytical chemistry approaches and next generation sequencing of microbial genes has been applied to bog and fen habitats in the Marcell Experimental Forest (MEF), northern Minnesota. Chemical and spectroscopic analyses of soil organic matter (SOM) in the solid phase peat from different sites throughout the MEF identified three distinct zones within the peat core each with unique properties: (1) a poorly decomposed surface portion; (2) a more decomposed middle section and (3) a more homogeneous and constant lower section. Solid phase FT IR , ^{13}C NMR and ^{31}P NMR spectroscopy data indicated shifts in abundance of different classes of compounds within each zone. Ultrahigh resolution (UHR) mass spectrometry and PARAFAC modeled 3-D excitation-emission matrix [EEM] fluorescence spectroscopy were used to identify the reactive and refractory dissolved organic matter (DOM) pools with depth in peat porewaters at each site. Radiocarbon signatures of microbial respiration products (dissolved inorganic carbon, DIC; CH_4) more closely resemble that of DOM rather than solid peat, indicating that carbon from recent photosynthate is fueling the majority of the decomposition. Microbial community structure, genes encoding plant polymer-degrading enzymes, properties of DOM, and numerous other variables show strong vertical stratification patterns. Surface peat, characterized by high DOC concentrations and relatively low aromaticity, harbored diverse and abundant bacteria and fungi. Bacterial communities were dominated by the Acidobacteria, Verrucomicrobia, and Proteobacteria phyla. The majority of phenol oxidase genes are assigned to Acidobacteria and Proteobacteria. In more decomposed and anoxic layers at 30-50 cm depth, anaerobic metabolic pathways and fractions of methanogens and syntrophic fermenters became elevated. The abundance of fungi as determined by qPCR of rRNA genes attenuates more rapidly with depth than do other domains, leading to bacterial and then archaeal dominance with depth below the surface. All domains show elevated abundance in the subsurface below 50 cm depth in the fen compared to the bog. The relative abundance of archaea increased with depth. Below 75 cm, methanogens were progressively replaced by uncultivated Crenarchaeota lineages that accounted for up to 60 % of the microbial community. The deeper peat shows a less dynamic microbial community, depressed exoenzymatic activity, and accumulation of more aromatic DOM compounds. Marked differences are observed in the active microbial community composition as determined from rRNA amplicon sequences in comparison to DNA-derived rRNA genes. Isotope mass balance indicates that processes other than methanogenesis (fermentation, anaerobic respiration) predominate in the deep peat leading to dominance of CO_2 production at depth. A multivariate linear model identified quantity and quality of DOM and surface vegetation as most significant variables governing microbial community turnover spatially and seasonally, and pointed to the dominant microbial groups and metabolic pathways associated with carbon and nutrient cycling in the peatland.

NAME: Lara Kueppers
ORGANIZATION: UC Merced
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Responses of subalpine tree recruitment to warming within and above current altitudinal ranges

ABSTRACT:

Research Objectives: Niche models and paleoecological observations indicate that climate change will alter the geographic distributions of plant species. An upward shift in the ranges of subalpine forest trees would displace alpine species and alter high elevation hydrology and carbon cycling. 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 (LSA), at upper treeline (USA), and in the alpine (ALP). We are using infrared heaters to increase growing season surface soil temperatures, and to lengthen the growing season. The warming treatment is crossed with a summer 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 limber pine (*Pinus flexilis*), Engelmann spruce (*Picea engelmannii*), and lodgepole pine (*Pinus contorta*). We are asking, (1) Will subalpine trees move into current alpine habitat as a result of climate change? (2) Will subalpine trees be impaired in their existing range as a result of climate change? And (3) What ecophysiological, population genetic, and/or biogeochemical factors influence climate-induced changes in subalpine species success within and outside their current ranges?

Results: During 2010-2012, the snow-free period was ~one month longer at USA than at either ALP or LSA; sites also differed by more than 6 m s^{-1} in average wind speed and 4.6 °C in daily mean temperature. ALP had higher soil moisture than USA and LSA, but had many days below 16% volumetric water content, a threshold observed to reduce seedling stomatal conductance. Heated plots have had higher soil temperature than control plot means, with larger increases (~4.5 °C) in LSA, than in ALP and USA (1.5-2 °C). Heating alone tended to slightly reduce soil moisture, even in ALP and USA, while HW plots were not systematically wetter or drier than control means, as intended by our original experimental design. In 2012, heating advanced site-average melt date by 10-40 days. Preliminary analyses of 2010-2011 seedling data show that heating reduced germination and initial seedling survival for two species and both populations in LSA, consistent with expectations of reduced recruitment at lower elevations with warming. At USA, heating effects were contingent on year and species, with increased limber pine but decreased Engelmann spruce germination with warming in 2010. In ALP, contrary to expectations of increased recruitment with warming, experimental heating did not increase germination or survival for any species or population. Soil moisture (5-10cm) was a covariate of seedling survival in 2010, with limber pine seedling photosynthesis stopping completely with soil moisture below 0.8 m^3/m^3; and survival correlated with number of days below 0.8 m^3/m^3 moisture across all sites. Further, Engelmann spruce survival to two years in treeline and alpine sites occurred only in watered plots. Taken together, these preliminary analyses suggest that warming may result in lower elevation range contraction but not upper elevation range expansion of subalpine trees in the absence of additional growing season soil moisture.

NAME: Marcy Litvak
ORGANIZATION: University of New Mexico
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Carbon and energy balance consequences of widespread mortality in piñon-juniper woodlands

ABSTRACT: 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 datsets 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 ~ 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 litter and course woody debris are slow to decompose in these semiarid environments, ecosystem respiration initially decreased following mortality, and only increased two years post mortality following a large monsoon precipitation event. We also used a high resolution (5 x 5 meters) remote sensing time series from the RapidEye satellite constellation acquired over both PJ woodlands to test how well the structural changes measured remotely by RapidEye related to the carbon fluxes measured *in-situ* with the flux towers. In the three 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.

NAME: Yiqi Luo

ORGANIZATION: University of Oklahoma

PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Evaluating and Improving Performances of Global Land-surface Models through Data Synthesis and Data Assimilation

ABSTRACT: The state-of-the-art global land models usually generate great uncertainties in their simulations of terrestrial biogeochemistry, making their projections difficult to be used by the public and policy makers. In the past few years, the ECOLAB (Ecology Laboratory) at the University of Oklahoma has made great efforts to evaluate and improve the model performances by multi-scale data syntheses and data assimilation. These efforts can be summarized into three areas. (1) Development of methods to identify sources of uncertainty in model intercomparisons. We have developed a traceability framework that decomposes the modeled ecosystem carbon storage capacity into a few traceable components. This framework is applicable to most land models to mechanistically explain their structural differences in the modeled carbon cycle. We have also developed a new analytical method to accelerate the spin-up of global land models. The method can reduce the computational cost of spinning up land models to steady states by >90%, and permits many global analyses that were impossible with traditional spin-up methods. (2) Data syntheses. We have revealed several fundamental properties of terrestrial carbon cycle in responding to environmental changes, which can be used to benchmark and improve the performances of global land models. For example, by analyzing observations from globally distributed eddy-flux sites, we found thermal optimality that optimal temperature of net ecosystem carbon uptake varies with annual mean temperature over years and across sites. We also found a counter-clockwise hysteresis pattern of net ecosystem exchange with temperature at most sites. We also have revealed the spatiotemporal variations of gross primary productivity (GPP) are jointly controlled by the length of carbon uptake period and seasonal maximum GPP. (3) Data assimilation. We have applied data assimilation to improve the performances of two global land models: the Community Land Model with Carnegie-Ames-Stanford Approach biogeochemistry module (CLM-CASA’) and Community Atmosphere Biosphere Land Exchange (CABLE) model. Assimilating observed soil carbon data (e.g., IGBP-DIS global gridded product) alone can greatly reduce uncertainty in model prediction of soil carbon. In general, our efforts on developing a general framework for model intercomparisons, data syntheses to reveal underlying mechanisms of carbon-cycle dynamics, and data assimilation for reducing uncertainties of model simulations will improve the performances of current global land models.

NAME: Kadmiel Maseyk
ORGANIZATION: University of California, Merced
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: COS Flux Measurements: New Instrumentation and Eddy Flux Observations for a Carbon Cycle Tracer at One-Millionth the Concentration of CO2

ABSTRACT: Atmospheric carbonyl sulfide (COS) is a promising new tracer for measurement-based approaches to constrain biosphere-atmosphere carbon and water exchange. As the uptake of COS and CO_2 by vegetation is closely coupled during photosynthesis, concurrent COS and CO_2 measurements have been proposed to separately quantify the terrestrial gross fluxes of photosynthesis and respiration at ecosystem to continental scales. We have explored the dynamics of COS ecosystem-atmosphere exchange in a wheat field at the Southern Great Plains ARM site using newly available instrumentation for trace gas research. Using Quantum Cascade laser technology and high resolution Tunable Infrared Laser Differential Absorption Spectroscopy (QC-TILDAS), the COS analyzer (Aerodyne Research) is capable of measuring COS concentrations at 10 Hz and with a 1 sec accuracy of < 5 ppt, as well as CO_2 and H_2O. This enabled us to make near continuous eddy covariance (EC) measurements of COS fluxes within a background atmospheric concentrations of ~ 500 ppt, which represent successful EC measurements from the lowest ambient concentration trace gas yet made. In addition, we coupled the QC-TILDAS to an automated soil chamber on a two-hourly cycle, providing us with unparalleled information on in situ soil COS flux behavior.

Measurements were made over a two-month period that covered the growing season, senescence and post-harvest periods. We found that during the growing season, there was a strong uptake of COS by the canopy of between ~ 10 and 40 pmol m^{-2} s^{-1}, with a strong diel signal. Ecosystem COS sink strength diminished as the plants approached the grainfilling period, and after senescence and over the harvested field, we observed a strong source of COS to the atmosphere of up to +40 pmol m^{-2} s^{-1}. Contrary to what is commonly assumed, we observed that overall the soil was a net source of COS, but both sink and source behaviour was observed in a strongly temperature dependent response. However, during the peak growing period, soil COS fluxes were only a few percent of the canopy COS uptake, and therefore not a significant source of error for using COS as tracer of gross carbon fluxes. Further investigations into the soil COS fluxes indicate that roots, not soil microbes, appear to be responsible for the COS production. We also observed COS production from grain heads. Therefore it seems processes associated with senescence and plant internal reallocation of resources underlie the interesting seasonal pattern of COS fluxes we observed. This information is now being incorporated into regional scale modelling and interpretation of boundary layer atmospheric COS concentration measurements. In this study, we have shown how these high-resolution COS measurements at high precision are opening up new opportunities for exploring and constraining carbon cycle processes. In addition they are providing new insight into system biogeochemistry and plant responses as revealed through trace gas production. Observations in a range of ecosystems are needed to compare and contrast these responses and identify the relevant parameters to include into terrestrial COS analyses and models.

NAME: Pat Megonigal

ORGANIZATION: Smithsonian Institution

PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Cryptic Methane Emissions from Upland Forest Ecosystems

ABSTRACT:

Background

There is evidence that upland ecosystems emit 36% as much methane to the atmosphere as global wetlands, yet we know almost nothing about this source. Earth system models will need to be refined in order to quantify CH_4 emissions from upland forests, and this requires a more nuanced understanding of the biogeochemical processes that govern upland CH_4 emissions. Our objectives were to test the paradigm that upland trees transpire methane, and test the biogeochemical assumptions of an existing global model of upland methane emissions.

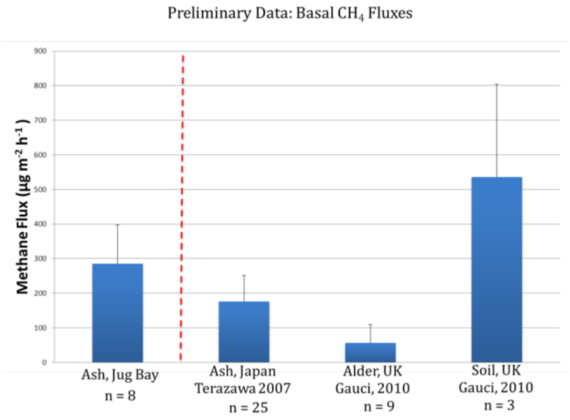
Methods

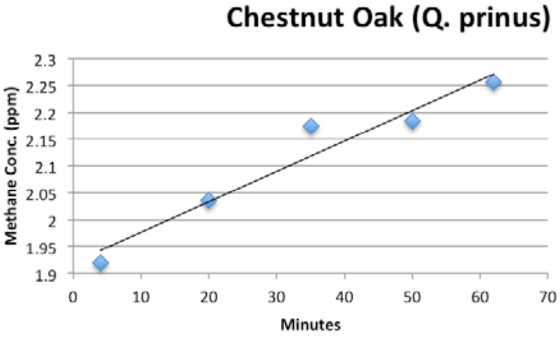
Transects were established in two temperate forests, each anchored on the dry end by upland forest and on the wet end by a forested wetland (Figure 1). At one site (SERC) the wet-end forest is saturated seasonally during the winter and dry during the summer, while at the second site (Jug Bay) the forest wet year around. We developed closed chambers to detect CH_4 emissions from the full range of tree diameters present at our site. Previous studies of methane emissions from trees have been biased toward small-diameter trees that account for a relatively small fraction of mature forests. The result is two versions of tree chambers, one for small-diameter stems and one for larger stems (Figure above). We are in the process of fitting chambers to the trees on each transect and present limited preliminary data below.

Results and Discussion

Methane emissions from *Fraxinus* spp. at Jug Bay in Sep 2012 were higher than similar species reported by Gauci et al. (2010), and 60% of soil emission rates from the same Gauci et al. (2010) study on an area basis (Figure right).

We attempted a flux measurement from one upland tree to test our methods. The *Quercus prinus* is located in a site where the water table is >30 cm deep during the wettest time of year (Jan-Mar) and soils clearly indicate the site is upland. Despite the fact that it was winter, we measured significant CH_4 flux from the stem of this tree, indicating that our design will be sensitive enough to detect the low emission rates that are expected in upland forests.





Gauci, V. et al. 2010. Woody stem methane emission in mature wetland alder trees. *Atmospheric Environment* 44:2157-2160

NAME: David Moore
ORGANIZATION: University of Colorado
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: The impact of Mountain Pine Beetle disturbance on carbon cycling in high elevation Western forests

ABSTRACT: Amid a worldwide increase in tree mortality, mountain pine beetles (Dendroctonus ponderosae Hopkins) have led to the death of billions of trees from Mexico to Alaska since 2000. This is predicted to have important carbon, water and energy balance feedbacks on the Earth system. Counter to current projections, we show that on a decadal scale, tree mortality causes no increase in total respiration from scales of several square meters up to an 84 km2 valley; rather we found comparable declines in both gross primary productivity and respiration suggesting little change in net flux, with a transitory recovery of respiration 6-7 years after mortality associated with increased incorporation of leaf litter carbon into soil organic matter, followed by further decline in years 8-10. The mechanism of the impact of tree mortality caused by these biotic disturbances is consistent with reduced input rather than increased output of carbon.

NAME: J. William Munger
ORGANIZATION: Harvard University, SEAS
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Analysis of forest growth in long-term data sets from the Harvard Forest

ABSTRACT: Forests in northeastern U.S. are currently significant carbon sinks as they continue to regrow on land that were cleared for agriculture up until the early 1900's. Understanding how long they will continue to sequester carbon is an important question for future carbon management. We have been analyzing the 20-year record of carbon fluxes and forest dynamics to better understand the interaction of climate and successional change to control the carbon balance of mixed deciduous forest. Red oak and red maple currently dominate the forest biomass at Harvard Forest. Red maples are an opportunistic, shade tolerant, relatively short-lived species, while red oaks are less shade tolerant, but long lived. Theory suggests that over time red maples should increase their dominance in mixed red oak-red maple stands. However, dendrochronology and growth increment data shows that maples are declining. To examine whether the maple decline is due to age-induced senescence or competition tree size and distance to nearest neighbors was analyzed on 3 stands; a control, a similarly aged logged site, and a younger stand. Historical patterns were examined by coring the same trees. Results show that the maples are capable of appreciable growth despite their age, but are suppressed by competition from nearby oaks. Disturbance events release red maples from this competition, resulting in increased growth. In spite of the decline in the canopy, the understory is overwhelmingly dominated by red maple, which suggests that although individual red maples are declining or dying, the current species distribution may remain stable; maples make up for short lifetime by having higher seedling survival. Retrospective analysis of carbon flux data for 1992-2010, seeks to determine the contributions of environmental factors to the observed trends and anomalies in Net Ecosystem Exchange. Annual NEE has nearly tripled over the time period, and the overall mean annual NEE (flux of CO2 from the atmosphere to the surface) is -3.07 Mg C ha-1 yr-1 with a range from -1.02 Mg C ha-1 yr-1 in 1998 to -6.44 Mg C ha-1 yr-1 in 2008. The environmental variables of air and soil temperature, precipitation, and light have large interannaual variability but no significant trends. Anomalies in NEE influenced by disturbances such as late frosts and drought can persist through the remainder of growing season or longer. The increased annual CO_2 uptake is due in part to increased growing season length; spring onset has been earlier and fall cessation has been later. Additionally the mean ecosystem response to temperature and PAR has changed over the 19 years, with the majority of the change happening during the growing season. Evaluation of this change points to changing physiology and ecosystem functioning driving the long-term trend in increased uptake. Neither the increased growing seasons nor the weather variations alone can account for the variation and trend in NEE. Increasing canopy efficiency suggests there has been an enhancement in foliar nitrogen or changing canopy composition, with possible small contributions from CO2 fertilization and water stress alleviation.

NAME: Sari Palmroth
ORGANIZATION: Duke University
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Quantifying the impact of nighttime transpiration on the magnitude of hydraulic redistribution in an unmanaged forest ecosystem (Duke Hardwood site, NC)

ABSTRACT: Plants lose water from leaves to the atmosphere as an unavoidable cost of allowing CO_2 diffusion to the carboxylation site. A portion of the water taken up during daytime from surface soil layers is made of water redistributed by roots during nighttime from deeper to shallower layers of the rooting profile. However, nighttime water loss may interfere with the hydraulic distribution (HR), potentially decreasing transpiration and photosynthesis. Both tree water uptake and HR in the soil are driven by variations in water potentials and resistances along the soil-plant-atmosphere continuum. The first decade of the 21th century was the warmest on record, and by 2050 the global average surface temperature is predicted to increase 2-4°C, with larger increases projected for the summers in most latitudes. In northern latitudes, nighttime temperatures are expected to increase more than daytime temperatures. Because relative humidity is not projected to change markedly, this may lead to higher nighttime evaporative demand (vapor pressure deficit, VPD). Although plants are expected to close their stomata at night to conserve water when carbon uptake is not occurring, there is growing evidence for relatively high nocturnal leaf stomatal conductance (g_{sN}) driving nighttime sap flux (J_{sN}) in many C_3 species. Nighttime sap flux (water uptake), can limit HR because the two processes compete for the same water. We studied the magnitude and among-species differences in $J_{sN,}$ and its potential impact on HR in a oak-hickory forest using sap flux measurements and a process-based model MuSICA. We hypothesized that environmental conditions can cause significant nighttime transpiration, the magnitude of which might be sufficient to delay the onset of HR.

At this forest, mean nightly VPD was >0.4 kPa 23% of the time. In some species J_{sN} increased with nighttime VPD in a saturating fashion, and represented 10–20% of daytime estimates. For diffuse porous species, the proportion of J_{sN} from the total daily J_s was constant over a range of tree sizes, but the proportion increased with tree size for ring porous species, indicating different hydraulic adjustments to increasing tree size between the two species groups. Furthermore, J_{sN} varied with soil moisture, showing higher sensitivity when soil moisture was low. In some cases, g_{sN} was more sensitive to VPD than daytime g_s, but large differences were observed among species. Simulations with MuSICA demonstrated that when J_{sN} is high, comparable to our estimates of J_{sN}, trees (filling storage for daytime use) and the atmosphere are the strongest sink for soil water, owing to a greater water potential gradient between deep soil and the plant than between different soil layers; as a result HR to upper soil layers decrease by more than 30%. Current VPD is therefore sufficient to drive significant J_{sN} and reduce the magnitude of HR. Stands composed of species with high J_{sN} are expected to have lower soil moisture in the upper soil, transpiration, and photosynthesis than stands with low J_{sN}.

Keywords: hydraulic redistribution, MuSICA model, night transpiration, sap flux, soil water content.

NAME: Shannon Pelini
ORGANIZATION: BGSU
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Open-top warming chambers reveal contrasting ecological responses of high and low latitude arthropod populations and communities

ABSTRACT: We are grateful for funding from TES, DE-FG02-08ER64510

Long-term experimental field manipulations that directly test the predictions about organisms' responses to climate change across latitude are lacking. This field experiment uses octagonal, 5-m-diameter (c. 22 m^3) open-top chambers to simulate warming at a high (Harvard Forest, Massachusetts) and low (Duke Forest, North Carolina) latitude hardwood forest site. **Our objective was to identify the effects of warming on ant and other arthropod populations and communities near the edges of their ranges.** Each site has 12 plots containing open-top chambers that manipulate air temperature incrementally from ambient to 6 °C above ambient.

These open-top warming chambers have been running for 3 years, and in that time we have found that the responses of arthropods to warming do, in fact, have a strong geographic signal, and variation in thermal tolerance is a good indicator of individual species' responses to warming. Overall, our results suggest that ants living in historically warmer, less variable locations are at greater risk of overheating with climate warming, even after accounting for spatial heterogeneity in warming effects, i.e. greater warming at high latitudes. More specifically, at our low latitude experimental site, where environmental temperatures exceed some ants' upper thermal tolerances (CT_{max}), ants with higher CT_{max} increased in density with warming; however, at the high latitude site, where environmental temperatures do not exceed CT_{max}, ants reach the highest densities in the warmest chambers regardless of their CT_{max}. Intraspecies variation in CT_{max} is also correlated with changes in foraging activity under warming.

Altogether, these changes in ant abundance and activity are not consistently accompanied by changes at the community level. We did see changes in individual species--15% of the species observed in the chambers at the high latitude site occurred fewer times (none occurred more) in warmer conditions, but there have not been changes in species diversity or composition. In contrast, although the same number of species responded to warming at the low latitude sites (but a smaller percentage), species composition did change and diversity decreased with warming. This supports other findings that ecological communities at low latitude sites may be more vulnerable to declines under warming, but additionally we found that individual species responded poorly, not favorably as expected, at high latitude sites as well. *Changes at the community level may take longer to manifest at high latitude sites, or the communities there may be more resilient to changes in individual species.*

NAME: Elise Pendall
ORGANIZATION: University of Wyoming
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Ecosystem phenology, restoration, and carbon cycling responses at the Prairie Heating and CO2 Enrichment Experiment

ABSTRACT: The Prairie Heating and CO2 Enrichment (PHACE) experiment has been ongoing since 2006 in native grassland near Cheyenne, Wyoming. Climate change has multiple, interacting effects on ecosystem processes that will influence future grassland sustainability. Prior results showed that plant biomass has responded to future climate conditions by increasing growth, especially of C4 plants, and in years of average or low precipitation. Net carbon losses have been observed consistently on elevated CO2 + warming plots. Elevated CO2 and warming increase plant community greenness and the potential for CO2 uptake early in the growing season, but have a generally negative effect later in the growing season. However, the magnitude and direction of greenness responses to climate treatments appears to be mediated by seasonal precipitation inputs.

A sub-experiment has allowed us to assess grassland recovery from disturbance. Restoration success might depend on selection of species most suitable for environmental conditions of the future. Our initial assessment of establishment from seed in bare sub-plots showed a slight advantage of species from warmer and wetter regions of North American grasslands compared to species common to southeastern Wyoming, but no differences were observed among PHACE treatments.

Elevated CO2 increased belowground biomass and root mass loss rates while elevated CO2 plus warming produced roots that were longer, thinner, heavier and had greater surface area than in ambient conditions. Results from the PHACE experiment support findings from our recent metaanalysis of 110 studies across all ecosystems, which indicated that elevated CO2 significantly increased root length (+26.0%), root diameter (+8.4%), and fine root biomass (+27.7%). Microbial communities from elevated CO2 exhibited an increased ability to decompose soil organic matter (SOM) compared with those from ambient CO2 plots, and microbes from warming plots exhibited increased thermal sensitivity for respiration. These microbial physiology responses may help explain observed net C losses with elevated CO2 and warming. Overall, our first-year results provide insights that will improve predictions of how grassland ecosystems will mediate future climate-carbon feedbacks.

NAME: Rich Phillips
ORGANIZATION: Purdue University
PROGRAM AFFILIATION: TES

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

ABSTRACT: The processes that control soil organic matter (SOM) decomposition have traditionally been modeled as a function of temperature and to a lesser extent soil moisture. Recent research suggests that inputs of labile carbon (C) – through their effects on soil microbial activity – can mediate the SOM responses to environmental drivers. We sought to better understand how precipitation and temperature mediate the magnitude of such "priming effects", and whether consideration of priming effects can aid in developing more accurate representations of soil C dynamics in land surface 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.

First, we released model root exudate mimics semi-continuously into soils and measured microbial and SOM responses. Our results indicate that although an exudate solution containing low concentrations of sugars, amino acids and low molecular weight organic acids increased microbial respiration by 48% relative to water controls ($p=.007$), this effect was unaffected by temperature and precipitation ($p > 0.05$). Further, the enhanced microbial activity was insufficient to alter extracellular enzyme activities (and hence SOM decomposition) which responded to temperature and moisture changes but not exudate inputs.

In a second field experiment, we quantified the magnitude of recently-fixed root-derived C inputs to soil from plants in the BACE plots. To do this, we trained roots and mycorrhizal fungi or mycorrhizal fungi alone to grow into soil cores containing "C4 soils" which contain a unique isotopic signature relative to plants in these plots. Carbon inputs from roots and hyphae together were two orders of magnitude greater than those from hyphae alone, indicating that belowground C fluxes in these plots are dominated by root inputs. Notably, the magnitude of the root-derived C fluxes were positively correlated with microbial activities (e.g. net nitrogen mineralization), indicating that root exudates were likely fueling microbial release of nutrients from SOM.

Collectively, our preliminary results provide some of the first field-based estimates of the extent to which changes in soil moisture and temperature can directly and indirectly alter the size of the SOM pool via root-derived priming effects, and lay the groundwork for the development of more mechanistic and better predictive models of SOM decomposition under climate change.

NAME: William Pockman
ORGANIZATION: University of New Mexico
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Responses of pinon and juniper to rainfall manipulation: mechanisms of drought-induced mortality and the implications of long-term acclimation.

ABSTRACT: In 2000-2003, extensive drought-induced pinon mortality (> 90% at some sites) occurred in pinon-juniper woodlands in the southwest US while mortality of co-occurring juniper was low (< 25%). In August 2007, we began a rainfall manipulation study at the Sevilleta LTER to test the proposed mechanisms behind this differential mortality: 1) hydraulic failure – the complete loss of water transport due to xylem cavitation, 2) carbon starvation - energetic limitations associated with water stress and prolonged stomatal closure to avoid hydraulic failure, and 3) interactions among these two mechanisms and plant pathogens. We imposed four treatments spanning long-term precipitation extremes on twelve 40 x 40 m plots in a pinon-juniper woodland: ambient control, drought diverting 45% of rainfall using clear plastic troughs, cover-control to assess effects of plastic troughs without diverting precipitation, and irrigation of 4-6 19 mm events to increase growing season water availability. We measured soil moisture, air and soil temperature, and sap flow of target trees, with periodic measurements of plant water potential, canopy leaf area, leaf level gas exchange and non-structural carbohydrates (NSC).

In August 2008, pinon mortality began on the two hillslope drought plots with shallow soils and was complete by summer 2009. Starting in 2010, after three years of treatment, juniper in these plots exhibited progressive dieback leading to mortality. A hydraulic model parameterized with site data, indicated that in 2008 hydraulic limitations in both species were greater in the drought plots, with pinon experiencing the greatest reduction of conductivity, but did not predict outright hydraulic failure. Dying pinon in 2008 exhibited high levels of bark beetle activity and infection by xylem-occluding *Ophiostoma* fungi, potentially exacerbating the hydraulic limitation of drought by occluding the xylem. Growing season accumulation of foliar NSC was reduced in individuals of both species that died compared to ambient control trees. Although clear treatment differences were evident in the third, relatively flat, block with deeper soils, neither pinon nor juniper have exhibited drought related mortality until 2012. These data support the interdependence of hydraulic failure and carbon starvation in tree mortality.

The protracted-survival of both species on the flat block with deeper soils provided an opportunity to study the response of both species to precipitation anomalies of several years duration. On irrigation plots juniper, but not pinon, exhibited increased xylem vulnerability to cavitation but both species exhibited increased specific hydraulic conductance in stem xylem associated with larger tracheid diameters. Drought treatment led to decreased cavitation vulnerability only in juniper but no change xylem hydraulic conductance in either species compared to ambient controls. Juniper shifted its stomatal regulation of leaf water potential, closing stomata earlier in irrigated plots and at lower water potentials in drought plots. Pinon exhibited no change in stomatal regulation. These data suggest that the acclimation state of each species, driven by prevailing precipitation conditions in years preceding drought, may contribute to the conditions required to induce mortality during a drought event.

NAME: Sasha Reed
ORGANIZATION: U.S. Geological Survey
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: It's all connected: Linking above- and belowground dryland responses to climate change

ABSTRACT: Arid and semi-arid ecosystems cover ~40% of the 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 expected changes in climate will affect vascular plant and biological soil crust community composition and biogeochemical cycles (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). While some of the ecosystem responses we have observed to date were expected, many of the results have been surprising. For example, an increase in the frequency of small summer rainfall events reduced moss cover from ~25% of total surface cover to <2% after only one growing season. In addition, only recently have we begun to observe temperature effects on lichens and mosses, suggesting that the timescales at which climate change affects dryland organisms vary by the nature of the climatic change (e.g., temperature vs. precipitation effects) as well as by biocrust functional type. In addition, because biocrusts play a large role in dryland function, these data also provide the first direct evidence from the U.S. that rising temperatures could compromise dryland C cycling, soil stability, and energy balance through effects on biocrusts. We have also observed temperature-induced declines in vascular plant net photosynthesis rates in a common C_3 bunchgrass, but no such effect on deep-rooted shrubs or C_4 grasses. These results complement long-term monitoring efforts in the region that show a significant decline in C_3 grass relative abundance and no change in shrubs or C_4 grasses. In addition, we have observed a strong coupling between reduced C_3 grass net photosynthesis and soil CO_2 efflux occurring near the grass's base, suggesting that temperature could affect carbon balance not only through community composition shifts, but also through above- and belowground interactions between dryland biota. Taken together, these data (1) highlight the complexity in relationships between climate, organisms, and biogeochemical cycles in dryland ecosystems; (2) support the idea that climate change could greatly affect organisms living in relatively harsh arid and semi-arid environments and thus, in turn; (3) drive significant alterations to ecosystem composition and function.

NAME: Peter Reich
ORGANIZATION: University of Minnesota
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: B4WarmED: An open-air process-oriented experiment exploring southern boreal forest response to future climate warming and precipitation shifts

ABSTRACT: Boreal Forest Warming at an Ecotone in Danger (B4Warmed) is a manipulative open-air experiment begun in 2009 in northern Minnesota exploring key mechanisms related to terrestrial ecosystem response to future climate warming and precipitation shifts. In doing so it simultaneously addresses the potential for projected climate change to alter tree function, species composition, and ecosystem processes at the boreal-temperate forest ecotone. The experiment includes a total of 72 7.1m^2 circular plots in two forested sites, in open and closed canopy habitats, and focuses on responses of juveniles of 11 local tree species, the soil community, and related biogeochemical processes. In 2012, we installed and deployed event-based rain exclosures on 18 plots in the open canopy replicates of the warming experiment begun in 2009, to remove approximately 40% of rain events during the summer. The design is thus now an incomplete factorial, with 3 levels of warming x 2 levels of rain x 2 sites (only in open, total of 36 plots) and with 3 levels of warming x 2 sites x 2 habitats (total of 54 plots), with 18 of the 72 plots included in both experimental contrasts. Treatments include three target levels of simultaneous plant and soil warming (ambient, + 1.7 °C, + 3.4 °C) and either ambient or reduced rainfall.

Some patterns for 2012 (and across the 2008-2012 period) were consistent with hypotheses about responses of species co-occurring in southern boreal forest but with contrasting boreal versus temperate distributions. Boreal species, especially conifers, showed negative responses to warming of photosynthesis, survival and growth. Temperate broadleaves (oak and maples) by contrast tended to have neutral or positive photosynthesis, growth and survival responses. Other responses to warming though were similar across species- these included consistent shifts (acclimation) in the temperature response functions of photosynthesis and respiration, as well as an extended phenological growing season due to earlier leaf-out and later leaf-drop. These responses were generally similar across years, rather than being amplified or minimized over time. Current emphasis includes developing generalized temperature acclimation response functions (e.g., for photosynthesis, respiration, and phenology) to incorporate into ecosystem and land surface models, as such processes are currently inadequately addressed in such work.

At the ecosystem scale, we observed that warming (both levels) increased soil respiration in both sites in all years, for example by 18% in 2009, 25% in 2010, 17% in 2011, and 9% in 2012 in the +3.4 °C treatment. Soil CO_2 flux decreased significantly in the rain removal treatments in 2012, but rain removal did not decrease the magnitude of the stimulation of soil CO_2 flux by warming. Additionally, rising temperatures can affect plant performance indirectly by increasing nutrient availability in soil via accelerating microbial activities. To address this issue in isolation, we assayed the growth of three indicator plant species in soils removed from our experimental plots. Biomass was significantly increased in soils from the +3.4 °C warmed soils compared to the ambient plots, providing a clear indication that warming treatment modified soil processes in significant ways. Ongoing assays of soil microbial and microfaunal communities, and of related carbon and nitrogen cycling processes, will provide insights into the mechanisms underlying these belowground responses.

NAME: Sigrid Resh
ORGANIZATION: Michigan Technological University
PROGRAM AFFILIATION: TES

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

ABSTRACT: Globally, soils store twice as much carbon (C) as the atmosphere, with forest soils comprising about a third of this soil C pool. Changes in the rate at which soils store or lose carbon could either attenuate or exacerbate increases in atmospheric CO_2. As such, mechanisms mediating soil organic carbon (SOC) sequestration in the face of an altered climate predicted for the future have been the focus of much study in recent decades. However, even with recent advances in the collective mechanistic understanding of soil processes, integrative studies tracing input pathways and biological fluxes within and from soils are lacking. The objective of this study is to assess interactions among different fungal decay pathways, wood quality, soil texture, soil temperature, and initial contact with mineral fractions (i.e., buried versus surface placement of wood) in stabilizing wood-derived C in soil. The use of ^{13}C-depleted woody biomass harvested from the Rhinelander, WI free-air carbon dioxide enrichment (FACE) experiment affords the unique opportunity to track the fate of wood-derived C as it is transformed into CO_2, dissolved organic carbon (DOC), and soil C pools derived from two distinctly different fungal decomposition pathways.

Six aspen sites were cleared to deploy a series of field decomposition experiments to investigate the stabilization of FACE wood C in soils. The research experiments include the following treatments: soil texture (sand, loam), wood quality (wood grown in $+CO_2$, $+CO_2+O_3$, and ambient atmosphere), fungal inoculation (white-rot, brown-rot, and natural rot), wood location (buried in the mineral soil vs. surface application), temperature (warmed via open-topped chambers and ambient), and no-wood controls. To compare the C dynamics of different treatments, stable carbon isotope techniques are being used to distinguish wood-derived C in CO_2, DOC, SOC, and SOC density fractions.

Progress to date includes: 1. Transported (from WI-FACE site to Michigan Tech) and chipped over 2700 kg of wood; 2. Created white rot (*Bjerkandera adusta*) and brown rot (*Gleoephyllum sepiarium*) fungal cultures to inoculate wood chip treatments; 3. Inoculated and incubated wood chip treatments for 3 months to ensure colonization; 4. Cleared six sites (1600 m^2 each) of all woody stems and established plots; 5. 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; 6. Deployed inoculated chips on treatment plot on surface or buried 15 cm in soil profile; 7. Instrumented treatment plots with lysimeters and temperature data loggers; 8. Fabricated open-topped chambers (OTC) for deployment to field sites when snow melts; 9. Initiated laboratory incubations to test the effect of wood quality and fungal inoculation on CO_2 flux rates and isotopic signatures of wood and CO_2.

Initial conditions for soil $\delta^{13}C$ 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 elevated CO_2, and elevated $CO_2 + O_3$ FACE treatments had average $\delta^{13}C$ values of -39.5 ‰ (se 0.10). The >12 ‰ isotopic difference between the soil and wood chip $\delta^{13}C$ values provides the basis for tracking the wood-derived C through the early stages of decomposition and subsequent storage in the soil. Early results from our laboratory incubations indicate that fungal pathways have an impact on both the C flux rates from the wood chips and difference between the respired CO_2 and wood chip isotope signatures.

NAME: Karina Schafer
ORGANIZATION: Rutgers University
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Hydrological response of an upland oak/pine forest on the Atlantic Coastal Plain to drought and disturbance

ABSTRACT: During 2005-2011, sap flux measurements were used to quantify transpiration, eddy covariance was used to quantify evapotranspiration, and a local water balance was derived though stream discharge data from the USGS. The forest experienced defoliation by Gypsy moth (*Lymantria dispar* L.) in 2007, a partial defoliation in 2008 and drought conditions in 2006 and more severely in 2010.

From 2005-2011, annual canopy tree transpiration (E_C) averaged 201 mm $a^{-1} \pm$ 47 mm a^{-1}. In this forest, E_C was reduced by 20% in 2007 when a defoliation event occurred compared to the seven-year mean from 2005-2011. Likewise during drought years in 2006 and 2010, stand transpiration was reduced by 8% in the month of July in 2006 and by 18% in 2010 compared to the seven-year mean for July. During the month of July in 2007 after the defoliation and subsequent re-flushing of leaves, E_C was reduced by 25%, even though only half of the leaf area re-flushed. Therefore, prolonged drought had a lesser effect on E_C as reduced foliage or episodic defoliation suggesting access to deeper soil moisture. Alternatively, this stand may experience higher sensitivity to drought because of the history of prior defoliation as seen in the higher reduction of E_C in 2010 compared to 2006.

Stream water discharge scaled to the watershed area showed greatest correlation with transpiration in a 24-day and a 219-day time lag, signifying hydrological connectivity on the watershed scale. The stream and transpiration undergo similar fluctuations coinciding with leaf on and leaf off conditions accounting for the capacity of the system. Thus, any changes in transpiration or precipitation will also alter stream water discharge and therefore water availability. Under future climate change, frequency and intensity of precipitation and episodic defoliation events may alter local water balance components in this upland oak/pine forest.

NAME: Karina Schafer
ORGANIZATION: Rutger University, Newark
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Impacts of fire intensity on water use efficiency and photosynthetic capacity in an upland oak-pine forest

ABSTRACT: With increasing population densities in rural, forested areas, prescribed fire has become a vital tool in limiting wild-fire destruction. While this technique offers much in means of fire prevention, it also has subsequent ecological effects. Previous studies have looked at the effects of these fires as a disturbance regime, however, none have had the data to conduct a comparative analysis of these fires based on intensity. Therefore, a comparative analysis of the affects of fire of varying intensities on physiological differences of over-story trees in a Northeastern oak/pine and pine forest was conducted. To achieve this, sap-flow rates where monitored in conjunction with photosynthetic measurements of *Pinus rigida* on three sites, Brendan T. Byrne (BTB), Cedar Bridge (CB), and Silas Little (SL), whereby CB and SL are Ameriflux sites. Each study site had two sap-flow monitoring stations, one within the disturbed site of a prescribed burn (FS), and one within a control site (CS) that was not burned. The data was collected between 2011-2013, where each site was burned once, on different years. The most intense fire, BTB, was conducted in March 2011, while SL, the least intense fire was conducted in February 2012. The most recent fire, with an intermediate intensity, was conducted in March 2013 at CB. Immediately following the most intense fire, photosynthetic rates increased in the FS. However, by the following summer of 2012, any effects of the fire had diminished, and the photosynthetic rates of both the CS and FS were not significantly different. The sap-flow rates in the FS of BTB were also subsequently higher than the CS after the occurrence of the fire, and remained so until April 2012. Furthermore, at SL, the photosynthesis parameters were increased in the FS directly following the fire. The effects of the fire were prevalent throughout the first summer following the fire, where the FS had higher photosynthetic rates than the CS. While the photosynthetic rates where effected by the fire, no increase in sap flux was measured at SL FS.

NAME: Karina V.R. Schäfer
ORGANIZATION: Rutgers University
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Exploring the influence of time and spatial resolution on the prediction of latent heat fluxes

ABSTRACT: Predicting latent heat flux in forests is essential to understanding the hydrological cycle. However, this is not an easy task. Plant transpiration constitutes a considerable fraction of the water vapor flux above canopies and it depends not only on soil and atmospheric conditions, but also on how different species respond to environmental stimuli. In this work we explore the influence of time and spatial resolutions on the quality of the predictions of latent and sensible heat fluxes using OLAM, a global land-atmosphere model with powerful local mesh refinement capabilities. Our evaluation of simulation results against eddy covariance tower measurements showed that, despite difficulties on predicting the daily variation of the latent heat flux, the big leaf approach employed in our runs successfully estimated monthly evaporation totals for the studied period, which ranged from July 2009 to 31 October 2009.

Our sap-flow observations displayed features at daily and intra-daily time scales that are currently not well represented by OLAM. Among them, we emphasize the diurnal dynamic patterns of transpiration, in which the vegetation adjusts its transpiration rates to decreased soil moisture by shifting towards the morning and increasing stomata resistance at the afternoon. While some species, such as red maple show a next-day response to precipitation and strong morning-bias when soil is dry, other species such as red oak take longer to respond to increased soil moisture (4 days) and show diurnal transpiration dynamics that is less sensitive to soil moisture. We suggest that the simplified stomata parameterization employed in the big leaf approach which does not include the mechanics of water transport through the tree system is not capable of predicting the morning-time bias of intra-daily patterns of evaporation, nor is it able to differentiate between the species' specific response to environmental conditions, such as declining soil moisture. We show encouraging results obtained with Finite Element Tree Crown Hydrodynamics (FETCH) model, which, upon coupling with an ecosystem model such as ED2 could be used to reduce the gap between our predictions and observations of daily and intra-daily latent heat flux at local scales.

NAME: Edward Schuur
ORGANIZATION: University of Florida
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Effects of experimental warming of permafrost on ecosystem carbon balance in Alaskan tundra

ABSTRACT: 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 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 (winter warming) and open top chambers to increase growing season air temperatures (summer warming). We show that experimental warming that caused permafrost degradation led to a two-fold increase in net C uptake by the ecosystem during the growing season, in line with decadal trends of 'greening' tundra across the region[11-13]. However, warming also enhanced winter respiration, which entirely offset growing season C gains. Winter C losses may be even higher in response to actual climate warming, and in that scenario, could be expected to more than double overall net C losses from tundra to the atmosphere. 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 the same location.

NAME: Julie Shoemaker
ORGANIZATION: Harvard University
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Environmental drivers of whole-ecosystem methane fluxes from a lowland evergreen forest.

ABSTRACT: Forests dominate the global carbon cycle, but their role in methane (CH_4) biogeochemistry remains uncertain. Limitations in mesoscale sampling approaches have led to gaps in our knowledge of the CH_4 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 CH_4 cycle. Because CH_4 is a more potent greenhouse gas than carbon dioxide, quantifying the role of various forests in global CH_4 biogeochemistry is necessary to determine their net climate influence. Recent improvements in laser CH_4 analyzers have allowed for their use in combination with eddy covariance (EC) techniques, giving us the ability to fill in this knowledge gap. We examine a time series of EC-derived CH_4 fluxes, obtained over 2 years from Howland Forest, a lowland evergreen forest in central Maine. During the summer months of both 2011 and 2012, this forest was a small positive source of CH_4 to the atmosphere, averaging between 1-3 nmol m^{-2} s^{-1}. During 2011 (a wetter than average summer) positive fluxes continued through November, while in 2012 (a drier, more typical summer) the forest transitioned from source to sink for CH_4 during early August. Using both linear modeling and a neural network approach, we find gross primary productivity (GPP) and soil moisture at 10cm to have the strongest explanatory power over the trends in the CH_4 flux data. We observe that the relationship between CH_4 flux and its environmental drivers differs during high and low water table conditions, indicating threshold-type behavior. Wavelet analysis shows intermittent coherence between the CH_4 data and GPP data at approximately 24 hrs during the summer and fall, consistent with GPP being the strongest correlate of CH_4 emissions when water is not limiting. Overall, these results show that certain forest types, such as this lowland evergreen site, may be net sources of CH_4 to the atmosphere during wet years, while remaining weak sinks during average to dry years. This has important implications for assessing the forest's net climate impact, and suggests that there may be a positive feedback with forest methane emissions and climate change at this site.

NAME: Melinda Smith
ORGANIZATION: Colorado State University
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Low resistance but high resilience of a grassland ecosystem to Dust Bowl magnitude drought

ABSTRACT: Forecasts for increasing intensity and frequency of climate extremes with global climate change suggest that events such as severe droughts will play a greater role in determining future ecosystem function and dynamics. However, the rarity and unpredictability of climate extremes has limited our ability to assess the mechanisms governing their impacts on ecosystems. We experimentally imposed a two-year drought of 1930's Dust Bowl magnitude in a central US grassland and found that ecosystem function (aboveground net primary productivity) was reduced far below any observed level in almost three decades. Differential sensitivity to drought among the co-dominants representing key plant functional types (PFT's; C4 grasses, C3 forbs) led to low ecosystem resistance, and re-ordering of the co-dominant species. Despite altered community composition, recovery in function occurred one year post-drought due to compensation by the C4 grass dominant for the loss of the C3 forb dominant via rapid demographic responses. Thus, while extreme drought led to alterations in abundance of dominant PFT's, this compositional re-ordering enhanced ecosystem resilience.

NAME: Neil Sturchio

ORGANIZATION: University of Illinois, Chicago

PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Biophysical drivers of CO2 and CH4 emissions from moist acidic tundra upon experimental warming

ABSTRACT: Arctic tundra ecosystems are experiencing structural and functional changes due to climate warming and associated changes in winter precipitation. Greater snow cover in the Arctic provides soil thermal insulation and induces vegetation changes that may affect the vulnerability of stored C. Higher mineralization of centurial C in forms of CO_2 or CH_4 emissions may cause positive feedback with the climate system. Specifically, vegetation shifts favoring ecosystem productivity and associated alterations in thermal and hydrological regimes with warming may trigger CO_2 and CH_4 emissions. Therefore, the CO_2 and CH_4 forms of C emission are relevant to climate models, but the biophysical mechanistic understanding of these warming-C cycling feedbacks is currently lacking for Arctic tundra. We measured O_2, CO_2 and CH_4 soil gas concentrations and fluxes over a growing season adjacent to a snow fence (to mimic predicted increases in snow cover) located in moist acidic tundra at Toolik Lake, AK. To account for soil physical changes that may affect gas diffusivity we also measured the ^{222}Rn flux. We found that this site may switch from being CH_4 neutral to being a source of CH_4 with warming. In contrast, CO_2 efflux did not appear to be sensitive to increases in soil temperature, likely because of reduced gas diffusion coefficients under enhanced winter precipitation. Reduced diffusion of O_2 into the soil may have prompted the large production of CH_4, although ecosystem CH_4 emission was limited by diffusion. The $\delta^{13}C$ value of CH_4 also indicates a progressive increase in the prevalence of methanogenesis by the CO_2 reduction pathway relative to acetate fermentation with increased winter soil thermal insulation. Methanotrophy appeared to be limited by redox changes at shallow depths within the experimental treatment sites. Our findings indicate that biophysical factors affecting gas diffusion drive CO_2 and CH_4 dynamics in Arctic moist acidic tundra.

NAME: Jim Tang
ORGANIZATION: The Ecosystems Center, Marine Biological Laboratory
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Stem respiration and its connection with soil respiration in a temperate forest

ABSTRACT: 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.

Our preliminary results indicate that the magnitude of stem respiration based on stem area was at the same order as soil respiration based on ground area. 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.

NAME: Kristina Teixeira
ORGANIZATION: Smithsonian Institute
PROGRAM AFFILIATION: TES
ABSTRACT TITLE: Savanna and an annual grassland in the Mediterranean climate of California

ABSTRACT: 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. To improve understanding of how forest recovery dynamics are shaped by climate and may be impacted by climate change, we are creating a comprehensive database on C cycling in secondary forests and using it, together with biogeochemical process modeling, 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 CO_2 and climate will affect patterns of forest recovery. A review on the subject (Anderson-Teixeira et al. 2013; GCB) indicates that the dynamics of forest recovery are sensitive to climate and are being impacted by increasing atmospheric CO_2 and changing climate. Rates of forest recovery generally increase with CO_2, temperature, and water availability. Drought reduces growth and live biomass in forests of all ages, having a particularly strong effect on seedling recruitment and survival. Responses of individual trees and whole-forest ecosystems to CO_2 and climate manipulations often vary by age, implying that forests of different ages will respond differently to climate change. Furthermore, species within a community typically exhibit differential responses to CO_2 and climate, and altered community dynamics can have important consequences for ecosystem function. Age- and species-dependent responses provide a mechanism by which climate change may push some forests past critical thresholds such that they fail to recover to their previous state following disturbance. Ongoing data synthesis and modeling efforts are aimed at enhancing understanding of the interactive effects of forest age and climate change on carbon cycling.

NAME: Richard Wehr
ORGANIZATION: University of Arizona
PROGRAM AFFILIATION: TES

ABSTRACT TITLE: Partitioning CO_2 fluxes with isotopologue measurements and modeling to understand mechanisms of forest carbon sequestration

ABSTRACT: 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 sequestration at the Harvard Forest by integrating stable carbon isotope analyses with a suite of measurement approaches including eddy covariance, soil chambers, plot trenching, and minirhizotrons. The data are being integrated in—and used to refine—the Ecosystem Demography 2 (ED2) model.

Here we present key results to date. Using eddy covariance measurements of the forest-atmosphere exchange of $^{12}CO_2$ and $^{13}CO_2$, we partitioned the net ecosystem CO_2 exchange (NEE) into photosynthesis and respiration on an hourly timescale—a longstanding goal in carbon cycle science. Photosynthesis (and canopy-integrated stomatal conductance) showed a linear response to sunlight with no evidence of saturation, but the slope of the linear response increased with cloudiness, presenting the illusion of saturation. The response of stomatal conductance to light was the same throughout the day and throughout the year despite large changes in atmospheric and soil moisture. Ecosystem respiration was relatively constant throughout the day and night but varied greatly with the flux tower footprint. Our analyses suggest that ecosystem heterogeneity around the flux tower contributes substantial bias to eddy covariance measurements of NEE, as well as to standard predictions of ecosystem photosynthesis and respiration.

The isotopic compositions of photosynthetic assimilation and belowground respiration imply that the effective age of the substrate for belowground respiration was about 2 weeks. The isotopic composition of belowground respiration showed little or no diel cycle but varied by 1 ‰ over distances as short as 2 m, perhaps due to the heterogeneous distribution of roots; flux tower measurements indicated that the magnitude of variation did not increase at larger spatial scales. Fine root production peaked in early June and again in mid September. Root nonstructural carbohydrates decreased from mid May to July, coinciding with increases in root production and respiration. Fine root turnover time ranged from 4.5-16 years. We trenched one of our two chamber plots in late 2012 to help investigate the role of roots in 2013.

Finally, we have developed a new version of ED2 that simulates the carbon isotopes. Driven by our measurements, this model will be used to explore the implications of ecosystem carbon allocation mechanisms for carbon sequestration and feedbacks to climate.