

UNIVERSITY - SBR ABSTRACTS

Evaluating Trace Metal Limitations on Methane Fluxes in Terrestrial Ecosystems

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The greenhouse gas methane (CH₄) is produced in terrestrial ecosystems by subsurface microbial carbon cycling under anaerobic conditions. Its formation is localized at terrestrial-aquatic interfaces such as wetlands, permafrost soils, and soil microenvironments where oxygen is limited and organic carbon is available. Global climate models predict higher CH₄ emissions from wetlands in the future because of an increase in inundated area and the enhancement of CH₄ production as temperature increases. The large radiative forcing induced by increasing atmospheric CH₄ concentrations makes it critical to understand the environmental controls on CH₄ production.

Global models of methane biogeochemistry assess CH₄ fluxes at the grid cell level by accounting for microbial respiration rates and how these rates are affected by temperature, pH, and soil redox state. Temperature is a major control on CH₄ production, and recent work has shown that methanogenesis in terrestrial ecosystems displays a high activation energy, indicating that increasing temperature will result in a substantial increase in CH₄ emissions from wetlands. However, it has also been shown that this relationship over predicts the temperature response of CH₄ production in many systems, suggesting that other substantial limitations on methanogenesis are present. A potentially important limitation that has been largely overlooked is trace metal availability. Methanogens are unique in having high enzymatic requirements for trace metals (e.g., Ni, Co, Zn, and Mo). Laboratory studies, primarily involving pure cultures of methanogens or anaerobic bioreactors, have shown that limited availability of trace metals inhibits methanogenesis, but such limitations have not been investigated in the field.

We hypothesize that trace metal limitations are important controls on CH₄ fluxes in terrestrial ecosystems. To test this hypothesis, we have characterized the properties, CH₄ production potential, and speciation of trace metals in wetland soils from field sites in Missouri and Florida. Surface waters in these wetlands are low in trace metals, typically <0.05 μM, well below the 1 to 5 μM concentrations shown as optimal for methanogenesis in pure culture studies. Regional river waters and groundwaters, potential water sources for the wetlands, show similar suboptimal dissolved metal concentration. Initial microcosm studies reveal that the wetland soils from our sites show methanogenic activity when maintained under anoxic conditions. Assays of lipid biomarkers indicate the presence of substantial bacterial and archaeal communities, including marker indicative of methanogens. Solid phase characterization reveals trace metal concentrations in the soils on the order of 1 to 10 μg/g. Spectroscopic studies suggest that the native metal content is largely associated with minor detrital components (e.g., silicate minerals). Soils from both locations show a substantial binding capacity for metals that maintains low dissolved concentrations (<0.05 μM) except upon addition of exceptional metal loads. Soils from the Missouri site have greater binding capacity, and spectroscopic measurements show that metals added to these soils bind to thiol groups on organic matter. Binding occurs primarily to carboxylate groups in the Florida soil, accounting for its lower capacity for metals. These initial studies indicate that trace metal availability in the wetlands systems under investigation is far below optimal levels and suggests that methanogenesis at these sites may be trace metal limited.

A multiscale approach to modeling carbon cycling within a high-elevation watershed

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Although soils are the largest repository of carbon at the Earth's surface, the rates of soil carbon accumulation, transformation and release to the atmosphere and surface waters remain a key uncertainty in forecasts of global change. Within the soil environment, residual plant material is transformed into a continuum of organic products of variable accessibility and reactivity. At the watershed scale, averaging over a variety of these soil reaction networks may obscure critical processes; whereas individual soil profiles provide a limited window into the ensemble of pathways that ultimately determines carbon fluxes to the atmosphere and surface waters. To address how collections of spatially and temporally linked reaction networks are manifest at larger scales and the consequences of scale for process-based models, we are studying C fluxes from the soil profile (0.3 to 2 m²) to the watershed (85 km²) scale (0.005 to 0.1 m²) within the LBNL SFA East River, CO watershed study site.

At the watershed scale, concentration-discharge relationships show considerable hysteresis, with dissolved organic carbon (DOC) fluxes dominated by the seasonal peak in discharge associated with snowmelt. The hysteresis behavior remains remarkably similar for DOC across multiple years. Evaluation of sub-watershed solute dynamics indicates that hillslope aggregation controls solute delivery and increasing discharge is thus flushing DOC that accumulated in the shallow soil during the previous season. Soil profiles generally show decreasing total organic carbon with depth; however, the depth gradients and distributions of organic carbon functional groups vary markedly between different vegetation types (*e.g.*, conifer forest to meadow) and landscape position within one vegetation type (*e.g.*, crest to hillslope). Variability in the carbon distribution with landscape position suggests the importance of soil moisture relative to litter inputs. Soil incubations at variable moisture contents also demonstrate the dependence of CO₂ fluxes on moisture content, with respiration rates increasing with increasing soil moisture from 0 to 66% saturation, followed by a decrease as soils approach saturation. On-going work includes the development of reactive transport descriptions of carbon transformations and how they are mediated by water availability and soil mineralogy.

Collectively, our data suggest that seasonal hydrologic variations create a pulse of DOC to surface waters that temporarily starve the soil environment of labile DOC and provide sub-optimal conditions for heterotrophic respiration, creating a lag time between the hydrologic forcing and the metabolic response. As a result, modeling carbon transformations at the watershed scale will require coupling the temporal dynamics of vertical and lateral water transport with those of soil biogeochemical reaction networks.

The influence of plant and microbial exudates on radionuclide mobility in subsurface environments *University-Led Research under the SBR program*

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This project is part of Department of Energy, Experimental Program to Stimulate Competitive Research (EPSCoR) Implementation Grant “*Radionuclide Waste Disposal: Development of Multi-scale Experimental and Modeling Capabilities*”. The key issues to be addressed include identifying source terms for contaminants in geologic disposal scenarios, determining the chemical speciation of risk-driving radionuclides (*e.g.*, Np, Tc, Cs, U, I) within engineered waste forms and natural subsurface environments, delineating the biogeochemical and physical processes through which contaminant transport is manifested, and predicting contaminant mobility across wide temporal and spatial scales.

This presentation specifically addresses the influence of microbial and plant exudates on radionuclide mobility. The risk driving radionuclides ⁹⁹Tc, ²³⁷Np, ¹³⁷Cs, and ²³⁸U were selected to represent a wide range of geochemical behavior. We have examined the influence of a variety of factors on radionuclide mobility including ionic strength, pH, and the presence of microbial or plant exudates. Comparison of baseline distribution coefficients to distribution coefficients in the presence of ligands such as oxalate, citrate, riboflavin, and catechol showed that high ligand to nuclide concentration ratios produced enhanced mobility, dissolution of native uranium, increased sorption of neptunium and to a lesser extent technetium and minimal effects of cesium behavior. Ionic strength had the greatest influence on Cs partitioning which is consistent with Cs sorption via ion exchange.

Further experiments have examined the influence of plant activity on radionuclide uptake in hydroponic systems. We studied the changes in composition and rate of exudation of metabolites from roots of *Andropogon spp.* exposed to different forms of phosphorous (P) fertilization. Plants were initially grown with available forms of nutrients and were transferred to different nutrient treatments of varying P bioavailability. There were significant and consistent shifts in the metabolic profiles in roots within 36 hours after exposure to various nutrient treatments.

These studies provide insight into the potential effects of plant and microbial exudates on radionuclide mobility and provide necessary data for further miscible displacement experiments and numerical values for modeling efforts which will utilize a unique set of imaging tools to monitor radionuclide transport through soils in 2D and 3D.

Project: Radionuclide Waste Disposal: Development of Multi-scale Experimental and Modeling Capabilities. This material is based upon work supported by the U.S. Department of Energy Office of Science, Office of Basic Energy Sciences and Office of Biological and Environmental Research under Award Number DE-SC-00012530

Understanding Technetium Transport in Porous Media with Batch Geochemical Tests, 4D Emission Imaging Experiments and Modeling Studies

University-Led Research under the SBR program

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In this work key parameters controlling technetium (Tc) transport in porous media will be quantified and modeled. Particular focus will be on how transitions in redox state are related to the transport and fate of Tc in the environment. Fundamental geochemical controls have been investigated in equilibrium and kinetic batch sorption studies and have shown substantial differences under oxic versus anoxic conditions as well as in transitions between these conditions. It has also been shown that the amendment of the porous media with strong reducing agents, such as titano-magnetite nanoparticles, can substantially enhance the sorption behavior. This fundamental understanding was then transitioned to column-scale studies intended to investigate the interplay between geochemical conditions and the flow regime. Initial experiments focused on developing and evaluating a novel, one dimensional gamma-ray scanning system to monitor the distribution of Tc-99m within the column over time. While ^{99m}Tc was found to be a useful tracer for one-dimensional transport, we have further investigated the use of SPECT (single-photon emission computed tomography) for 4D (3D with time-lapse) emission imaging of ^{99m}Tc distributions within a column. The value of SPECT imaging, when combined with computed tomography scans of the material, is that it is possible to both image transport behavior in 3D and related this to the structural characteristics of the porous medium, such as preferential flow paths. We are implementing reactive transport models in COMSOL to both improve the design of SPECT imaging experiments as well as to understand how redox transitions affect the local mobility of Tc. One case study, for example, integrates our findings throughout the project by predicting the Tc concentration distributions we might expect in the vicinity of a redox active inclusion (i.e., a zone impregnated with titano-magnetite particles). The model clearly shows a dynamic interplay between the availability of oxygen and Tc reactants, which are controlled by the flow system, and the reactive zone in the column. SPECT imaging experiments are now being designed to validate these modeling results, which are parameterized based on the results of the batch and column experiments.

Project: Radionuclide Waste Disposal: Development of Multi-scale Experimental and Modeling Capabilities. This material is based upon work supported by the U.S. Department of Energy Office of Science, Office of Basic Energy Sciences and Office of Biological and Environmental Research under Award Number DE-SC-00012530

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

University-Led Research through SBR program

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The overarching objective of this work is to develop a thermochemical model of Pu sorption to minerals and sediments that incorporates aqueous and solid phase speciation, redox reactions, and the influence of organic ligands. This has been done using a suite of techniques including variable temperature batch sorption, x-ray absorption spectroscopy, quantum mechanical modeling, and isothermal titration calorimetry. In the final year of this project we have utilized the conceptual and quantitative models describing Np and Pu speciation in subsurface environments to describe the mobility of Pu in a series of field lysimeter experiments called the Radiological Field Lysimeter Experiment (RadFLEX) at the SRS. Analysis of effluent samples from field lysimeters after exposure to 3 years of natural rainfall showed no mobilization of Pu above detection limits. Furthermore, measureable concentrations of Np in the effluent were only found from lysimeters with Np(V) sources. Lysimeters containing Np(IV)O₂ did not have any measurable concentrations of neptunium in the effluent. These findings are supported by laboratory and computational investigations of the strong association of tetravalent actinide species with mineral surfaces. After coring several Pu bearing lysimeters, little transport of Pu had been observed and greater than 99% of the Pu appeared to have remained within the source. There was a greater downward migration of the Pu^VO₂(NH₄)(CO₃)(s) source after just 2 years in the field compared with previously observed transport from Pu(IV) and Pu(III) sources after 11 years in the field. This behavior is consistent with both the enhanced mobility of pentavalent actinides relative to other actinides as well as reduction of Pu(V) to Pu(IV) leading to formation of Pu(IV) surface complexes or Pu(IV) (hydr)oxide precipitates. However, as transport of Pu(V) sources was slightly greater than other oxidation states, it is likely that the slightly enhanced transport observed within the lysimeters is due to transport of Pu as Pu(V) prior to reduction to Pu(IV). In addition, the presence of organic matter decreased the mobility of Pu(V). Although further investigation is needed, this could be due to enhanced reduction of Pu in the presence of organic matter leading to increased sorption to minerals or complexation of Pu with organic matter associated with the bulk minerals. These field lysimeter observations highlight the importance of Pu reduction as a major factor limiting the environmental mobility of Pu in environmental systems.

COLLABORATIVE RESEARCH: NATURAL ORGANIC MATTER AND MICROBIAL CONTROLS ON MOBILIZATION/IMMOBILIZATION OF I AND PU IN SOILS AND WATERS AFFECTED BY RADIONUCLIDE RELEASES IN USA AND JAPAN

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¹²⁹I is among the top three risk drivers at DOE Low Level Waste or High Level Waste disposal sites (such as SRS) due to its perceived high environmental mobility, large inventory (high fission yield), high toxicity, and long half-life (16M years). Additionally, it is one of the key radionuclides driving uncertainty with the secondary waste generated from the waste-water treatment facility at the Fukushima Daiichi Nuclear Power Plant (FDNPP). ¹²⁹I exists as iodide, iodate, and organo-iodine. The human and environmental risks associated with Pu disposal, remediation, and nuclear accidents scenarios stems mainly from the very long half-lives of several of its isotopes. The SRS is holding one-third of the nation's Pu inventory. Release of Pu isotopes into the atmosphere and subsequent deposition on the Fukushima Prefecture after FDNPP accident has been reported.

Significant progress has been made over the last 10 years in understanding radioiodine chemistry in groundwater and waste streams as a result of our breakthrough in iodine species detection. This analytical method can detect stable or radioactive iodine at ambient concentrations using standard laboratory equipment. We have shown for the Savannah River Site, Hanford, and Fukushima, that each of the three iodine species has vastly different chemical properties, including their tendency to remain mobile, to adsorb to solids or co-precipitate. Ambient Pu concentrations and isotopic ratios were determined with ICP-MS and alpha spectrometry, in samples collected from both SRS and Fukushima Prefecture.

Sediment Pu concentrations in the SRS F-Area wetland were correlated to total organic carbon and total nitrogen contents and even more strongly to hydroxamate siderophore (HS) concentrations. HS was detected in the particulate or colloidal phases of the sediments but not in the low molecular fractions (< 1000 Da). Water-extractable Pu containing macromolecules were separated via isoelectric focusing (IEF) and assessed via ESI FTICR-MS. Results suggested the presence of HS functionalities in the Pu containing IEF extract. While HS is a very minor component in the sediment, its concentrations greatly exceeds that of ambient Pu. ^{239,240}Pu concentrations in soil samples with different land use types as well as iodine speciation in river water and rainwater northwest of the FDNPP were well correlated to soil organic matter (SOM) content. SOM concentrations and Eh were positively, and pH was negatively correlated to ¹²⁷I concentrations in surface water and rain samples.

Applications of Isotope and Noble Gas Analyses for Water Resources Management

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In the US, 306 billion gallons of fresh water are withdrawn annually from either groundwater or surface water, for domestic use, agriculture, industry or energy production. The relative importance of these sources varies by state, from 80% groundwater reliance in Kansas, to 97% surface water reliance in West Virginia.

Groundwater is a stable, but finite resource. Overdraft threatens groundwater resources if extraction rates exceed recharge. Noble gas and isotopic signatures in groundwater can reveal the recharge mechanisms and conditions. The threats of contamination of groundwater by agricultural land use or point sources can be evaluated from groundwater travel times determined by tritium-helium or other age tracers. A geostatistical analysis of nearly 4000 tritium-helium ages and noble gas concentrations analyzed at LLNL showed that recharge in southern California is dominated by river bank filtration, irrigation return flow, and managed aquifer recharge. Areas of young groundwater coincide with Hydrologically Vulnerable Areas, as independently determined by the State Water Boards.

Although surface water is annually renewed, its availability is seasonally variable and uncertain due to future climate and environmental change. An enhanced understanding of the response and subsurface storage of headwater catchments through water residence-time studies can improve drought-vulnerability assessments. Preliminary results of tritium analyses at the Southern Sierra Critical Zone Observatory show a disconnect between stream water and vegetation uptake in August. Streams discharge decade-old water, while plants transpire recent summer precipitation. “Banking” surface water in subsurface reservoirs provides an economical opportunity to increase the reliability of water supply. The application of water banking has been limited by a lack of knowledge of groundwater/surface-water interactions, recovery efficiency, and water quality concerns. Water recovery efficiency was studied at an Aquifer Storage and Recovery (ASR) well in Woodland (CA) using introduced xenon as a tracer. In this case, 95% of the xenon was recovered after extraction of three injection volumes. Xenon samples were analyzed on a LLNL-developed benchtop Noble Gas Membrane Inlet Mass Spectrometer (NG-MIMS), greatly reducing the cost and turnaround time compared to traditional noble gas mass spectrometry. An introduced xenon tracer experiment at an artificial recharge pond in Fremont (CA) demonstrated the subsurface travel time towards a drinking water production well met the public health criteria. These and other examples demonstrate the benefit of isotope and noble gas tracer studies for water resources research and management.

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Systematic Investigation of the Biogeochemical Stability of Iron Oxide-Bound Organic Carbon: Linking Redox Cycles and Carbon Persistence

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Our core hypothesis is that the degradation rate of soil organic carbon (OC) during aerobic-anaerobic redox cycles is governed by the amount of iron (Fe)-bound OC, and the ability of microbial communities to utilize OC as an energy source and electron shuttle for Fe reduction that in turn stimulates reductive release of Fe-bound labile dissolved OC. We have been testing our hypothesis systematically using model Fe-OC complexes, natural soils, and microcosm system.

We have initiated studies of the dynamics of Fe and OC in hematite-OC and ferrihydrite-OC complexes during redox reactions. We found that hematite-bound aliphatic C was more resistant to reduction release, although hematite preferred to sorb more aromatic C. Resistance to reductive release represents a new mechanism that aliphatic soil OC was stabilized by association with Fe oxide. To the other side, pyrogenic OC can facilitate the reduction of hematite, by enhancing extracellular electron transport and sorbing Fe(II). For ferrihydrite-OC co-precipitates, the reduction of Fe and release of OC was closely governed by the C/Fe ratio in the system. Based on the XPS, XANES and XAFS analysis, the transformation of Fe speciation was heterogeneous, depending on the conformation and composition of Fe-OC complexes. Fe-bound OC was more thermally resistant compared to free OC, indicating the strong impact of association with Fe on the conformation of OC. Other experiments examining the mobilization and degradation of Fe-bound OC by natural wetland soil microbial communities are underway.

For natural soils, we investigated the quantity, characteristics, and reactivity of Fe-bound OC in soils collected from 14 forests in the United States. Fe-bound OC contributed up to 57.8% of total OC in forest soils. Under the anaerobic reactions, the reduction of Fe was positively correlated to the electron accepting capacity of OC. We also have collected tundra soil from Toolik (Alaska), and started microcosm experiment for studying the response of OC stability and Fe redox reaction to climate change.

Our findings so far highlight the closely coupled dynamics of Fe and OC, with broad implications on the turnover of OC and biogeochemical cycles of Fe. For our next step, we will investigate the transformation of Fe and OC and dynamics of microbial community, when the model Fe-OC complexes and natural soils are exposed to anaerobic-aerobic transitions. Furthermore, the molecular- to microcosm-scale experimental studies will be integrated with model simulations.