SFA 2.0
2014 GOLDSCHMIDT ABSTRACTS

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1.0 SFA 2.0 ABSTRACTS

Reactive Transport Benchmarks on Heavy Metal Cycling
Session/Location/Date/Time: Poster board in Session 21b, Thursday @ 17:00 - 19:00

B. ARORA[1*], K.U. MAYER[2], C.I. STEEFEL[1], N.F. SPYCHER[1], S.S. SENGOR[3], D. JACQUES[4], AND P. ALT-EPPING[5]
[1]Lawrence Berkeley National Lab., Berkeley, CA, barora@lbl.gov (* presenting author)
[2]University of British Columbia, Vancouver, Canada
[3]Southern Methodist University, Dallas, TX
[4]Belgian Nuclear Research Centre SCK.CEN, Belgium
[5]University of Bern, Bern, Switzerland

Abstract Modeling metal fate and transport associated with sediment, tailings, and waste rock is often needed for the management of abandoned mines and remediation of mining-impacted areas. Although a variety of reactive transport models have been used to investigate acid rock drainage (ARD) and heavy metal cycling, a systematic model inter-comparison has not been conducted to date. This study presents two benchmark problems dealing with 1) the generation and attenuation of ARD, and 2) sediment-metal interactions in mining-impacted lake sediments.

The first benchmark problem focuses on comparing reactive transport simulations of sulfide mineral oxidation and attenuation of ARD in partially water-saturated mine tailings. This benchmark considers variably saturated flow, multicomponent solute transport, diffusion of oxygen and carbon dioxide in the gas phase, sulfide mineral oxidation, the dissolution of gangue minerals, and precipitation and re-dissolution of secondary mineral phases. Four reactive transport codes - CrunchFlow, Flotran, HP1, and MIN3P were used to evaluate this benchmark. Despite substantial differences in model formulations, favorable agreement was obtained between the various codes.

The second benchmark problem focuses on heavy metal cycling in mining-impacted lake sediments. A multicomponent biotic reaction network with multiple terminal electron acceptors (TEAs) is considered to simulate the reductive dissolution of ferrihydrite and release of trace metals. The model incorporates Fickian diffusive transport, kinetic and equilibrium mineral precipitation/dissolution, and equilibrium aqueous and surface complexation. Four reactive transport codes - TOUGHREACT, CrunchFlow, PHREEQC, and PHT3D were used to evaulate this benchmark. Favorable agreement was obtained between these codes. Simulations of a more complex scenario including sedimentation and compaction with CrunchFlow and TOUGHREACT were also compared with this benchmark. Slight deviations in model results can be explained by different formulations for compaction.

Prediction of the biogeochemical roles of uncultivated bacteria and archaea in the subsurface (Keynote)
Session/Location/Date/Time: 19g: Room 202, Wednesday @ 10:30 - 11:00

JILLIAN F. BANFIELD[1,2], CINDY J. CASTELLE[1], LAURA A. HUG[1], KELLY C. WRIGHTON[1], ITAI SHARON[1], CHRISTOPHER T. BROWN[1], ROSE S. KANTOR[1], ANDREA SINGH[1], BRIAN C. THOMAS[1], BIRGIT LUEF[1], LUIS COMOLLI[2], KENNETH H. WILLIAMS[2], PHILIP LONG[2], SUSAN S. HUBBARD[2]
[1]University of California, Berkeley; jbanfield@berkeley.edu cjcastelle@berkeley.edu, laura.hug@berkeley.edu, wrighton.1@osu.edu, itaish@berkeley.edu, ctb@berkeley.edu, rsgkantor@gmail.com, andrea.singh@berkeley.edu, bcthomas@berkeley.edu
[2] Lawrence Berkeley National Laboratory; birgit.luef@gmail.com, lrcomolli@lbl.gov, KHWilliams@lbl.gov, pelong@lbl.gov, SSHubbard@lbl.gov

Abstract Despite dramatic progress in microbiology over the past decades, vast knowledge gaps remain concerning the extent of diversity and functional capacities of organisms within the Domains Bacteria and Archaea. Also of particular note is a lack of information about the biology of subsurface environments, especially sediments, in part due to sample complexity and challenges associated with sample recovery. Further, subsurface enrichment in microbial members of candidate phyla (CP), which lack even a single cultivated representative, has prevented a comprehensive assessment of biogeochemical processes. In research carried out in an aquifer adjacent to the Colorado River in Rifle, CO, our team is combining geochemical measurements and time/depth series sampling with high-throughput metagenomic sequencing of whole community DNA, to link environmental processes with predictions of microbial metabolic potential. Importantly, even very low abundance members (below 0.1% abundance level) of highly complex communities containing thousands of species are included in this metabolic analysis. Striking findings include overall genetic novelty, prevalance of bacteria and archaea from CP and from phyla not recognized previously, and, within the CP from two domains of life, the predominance of fermentation-based metabolisms, likely symbiosis-based lifestyles, small cells, and small genomes. Data integration enables development of models that describe the flow of carbon through the communities, and can identify linkages between specific organisms and numerous biogeochemical cycles.

Iron and carbon dynamics during the reductive transformation of organic matter-rich Fe(III) oxyhydroxides (Invited)

Session/Location/Date/Time: 10f: Room 304, Friday @ 09:15 - 09:30

A. C. CISMASU[1*], K. H. WILLIAMS[1], P. S. NICO[1]
[1]Lawrence Berkeley National Laboratory, CA, USA
*correspondence: accismasu@lbl.gov; khwilliams@lbl.gov; psnico@lbl.gov

Abstract The association of organic matter (OM) with Fe oxyhydroxides is suggested to shield OM from biodegradation, in addition to impacting the reactivity, transformation rate, and transformation products of OM-rich Fe oxyhydroxides such as ferrihydrite. The impact of this association on the biogeochemical Fe and C cycles is not entirely understood, and may depend on the type of OM and Fe oxyhydroxide, or on the means of association, i.e., OM adsorption vs. formation of OM-mineral co-precipitates. In an attempt to gain insight into the behavior of naturally occurring OM-bearing Fe oxyhydroxides, we examined the *in situ* reductive transformation of natural biogenic ferrihydrite, and monitored changes in mineralogy, composition, and Fe and C speciation, using several synchrotron-based diffraction, imaging and spectroscopic techniques.

Organic matter-bearing ferrihydrite precipitates (C_{org}:Fe ~0.33) that exhibit twisted stalk structures typically produced by the iron oxidizer *Gallionella ferruginea* were sampled in August 2012 from artificially aerated groundwater wells at the Rifle, CO field site. During following months, groundwater conditions became reducing, and the mineralogy of the Fe(III) precipitates was modified *in situ* by April 2013, denoted by the appearance of Fe(II)/Fe(III) phases (e.g., hydroxycarbonate green rust). Despite these changes, the stalk morphology of the original precipitates was preserved, and STXM spectromicroscopy data indicate that stalks became enriched in Fe(II). Carbon K-edge NEXAFS spectra were interpreted according to synthetic Fe(III)/alginate and albumin co-precipitates, and show that the initial Fe(III)-rich stalks are rich in organic carbon, whereas stalk-associated OM appears to be partially altered, or desorbed as Fe(III) reduction proceeds. This suggests that mineral-associated OM is partly available as an electron donor. The presence of organic matter also appears to affect secondary ferrihydrite biomineralization, as previously shown for synthetic analogs [1], and these data may be useful for interpreting the behavior of natural Fe(III)/OM precipitates under comparable aqueous conditions.

[1] Shimizu, M. et al. (2013). *Environ. Sci. Technol. 47* (23), 13375–84.

Constraints from U and Sr isotopes on the hydrology of a alluvial aquifer at Rifle, Colorado

Session/Location/Date/Time: 23f: Room 318, Thursday @ 15:45 - 16:00

JOHN N. CHRISTENSEN[1]*, ALYSSA E. SHIEL[2], MARK E. CONRAD[1], KENNETH H. WILLIAMS[1], WENMING DONG[1], TETSU K. TOKUNAGA[1], JIAMIN WAN[1], PHILIP E. LONG[1], SUSAN S. HUBBARD[1]
[1]Lawrence Berkeley Natl. Lab., Berkeley, CA 94720 USA (*correspondence: jnchristensen@lbl.gov)
[2]Univ. of Illinois Urbana–Champaign, Champaign, IL 61820

Abstract The Rifle Site consists of a floodplain along the Colorado River that was remediated through the removal of surface material underlying former U-V mill tailings. The Rifle Site provides an excellent field laboratory for the study of the fluxes of water and carbon from the vadose zone to groundwater (LBNL SFA2.0). A network of monitoring wells, particularly a series of holes instrumented in the vadose zone, provide the opportunity to closely sample groundwater and vadose zone porewater both in space and time. In order to better understand the spatial and temporal variation of vadose zone interaction with groundwater within the Rifle floodplain and provide constraints for a Rifle hydrological model, we have analyzed the Sr isotopic compositions and $^{234}U/^{238}U$ activity ratios (AR) of groundwater, vadose zone porewater (sampled through depth-distributed lysimeters) and surface water including the Colorado River. Significant contrasts in $^{87}Sr/^{86}Sr$ and $^{234}U/^{238}U$ allow the identification of different sources contributing to Rifle groundwater.

Contour maps of groundwater $^{87}Sr/^{86}Sr$ show a general increase in $^{87}Sr/^{86}Sr$ across the floodplain towards the Colorado river, with two localized highs. Similarly, $^{234}U/^{238}U$ AR show a decrease across the floodplain, but with a much steeper gradient than $^{87}Sr/^{86}Sr$. Vadose zone porewater is characterized by high $^{87}Sr/^{86}Sr$ and Sr concentrations and falls at one end of a mixing line with Rifle groundwater suggesting that a significant portion (up to 20%) is contributed through vertical recharge on the floodplain compared to the upgradient watershed. An irrigation-return ditch cuts the site toward the eastern edge. Sr and U isotopic and concentration analyses of water from the ditch and from nearby monitoring wells indicate a significant hydrologic connection between the ditch and groundwater, constraining the nature of the boundary conditions for the Rifle hydrologic model.

Results so far suggest that Rifle groundwater Sr is strongly influenced by vadose zone porewater, while high U concentrations and low (near 1) $^{234}U/^{238}U$ AR are due to local U sources associated with aquifer sediments consistent with previous observations.

Coordination and redox chemistry of aqueous Fe(II) and dissolved organic matter
Location/Date/Time/Session: 19i: Room 202, Tuesday @ 16:30 - 16:45

Ellen Daugherty[1], Benjamin Gilbert[2], Peter Nico[2] and Thomas Borch[1,3]

[1]Department of Chemistry, Colorado State University, Fort Collins, CO, U.S.,ellen.daugherty@colostate.edu
[2]Earth Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA, U.S.
[3]Department of Soil and Crop Sciences, Colorado State University, Fort Collins, CO, U.S.

Coordination and redox chemistry of aqueous Fe(II) and dissolved organic matter
ELLEN DAUGHERTY[1], BENJAMIN GILBERT[2], PETER NICO[2] AND THOMAS BORCH[1,3]
[1]Department of Chemistry, Colorado State University, Fort Collins, CO, U.S., ellen.daugherty@colostate.edu
[2]Earth Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA, U.S.
[3]Department of Soil and Crop Sciences, Colorado State University, Fort Collins, CO, U.S.

Abstract Biogeochemical cycling of iron and carbon is dependent upon the molecular-level interactions between iron (Fe) and natural organic matter (NOM) in soil and water. Several studies have found evidence for strong Fe(III) complexation via carboxylic functional groups as well as enhanced reduction of NOM-bound Fe(III) at circumneutral pH [1, 2]. Less is known about the coordination and reduction-oxidation chemistry of Fe(II) in the presence of NOM. In particular, there extent to which NOM inhibits or enhances Fe(II) oxidation is still under debate. Resolving these questions is crucial to understanding the chemistry that determines the solubility, mobility, and bioavailability of iron in terrestrial and aquatic systems.

We studied the interactions of Fe(II) with various types of NOM, including Swanney River fulvic acid and Leonardite at pH 5–7. Oxidation of Fe(II) in anaerobic solutions of NOM indicated the presence of oxidizing functional groups that could be reduced by $H_2(g)$ in the presence of palladium. X-ray absorption spectroscopy (XAS) was used to investigate the molecular structure of iron complexes formed upon reaction of Fe(II) with reduced NOM. For the reference NOM types, Fe(II) complexation was dominated by carboxylic acid groups. Complexed iron exhibited faster kinetics of oxidation by O_2. For one hydrophilic fraction of subsurface pore-water NOM, extensive Fe(II)–thiol coordination was detected. These results demonstrate one mechanism for the enhanced rate of Fe(II) oxidation, and show that Fe(II)-NOM interactions are dependent upon the type of NOM

Additive Surface Complexation Modeling of Uranium(VI) Adsorption onto Quartz-Sand Dominated Sediments

Location/Date/Time/Session: 10d: Room 304, Tuesday @ 15:00 - 15:15

WENMING DONG[1*], JIAMIN WAN[1] AND TETSU K. TOKUNAGA[1]

[1] Lawrence Berkeley National Laboratory, Berkeley, CA 94720 USA (*correspondence: WenmingDong@lbl.gov)

Abstract Nuclear materials processing and U mining and milling resulted in many acidic U(VI) groundwater plumes during the Cold War. The F-Area of the Savannah River Site (SRS) in South Carolina (USA) is an example where groundwater has been contaminated by a large, persistent U(VI)-containing acidic plume during 1955-1988. Although many U(VI) contaminated aquifers (e.g., the F-Area) are composed predominantly of quartz-sand sediments, understanding of geochemical mechanisms governing U(VI) adsorption to quartz-sand dominated sediemnts under acidic conditions is still limited. We conducted U(VI) adsorption experiments using quartz-sand dominated plume sediments and reference minerals quartz, goethite and kaolinite. We developed a new humic acid adsorption method to determine the relative surface area abundances of individual minerals of the sediments. This method plays a key role in successful application of the mineral component-additivity (CA) based surface complexation modeling (SCM) for understanding of geochemical mechanisms governing U(VI) adsorption. Our experimental results indicate that quartz has stronger U(VI) adsorption ability per unit surface area than goethite and kaolinite at pH ≤ 4.0. Our modeling results indicate that the binary mineral (goethite/kaolinite) CA-SCM under-predicts U(VI) adsorption to the quartz-sand dominated sediments at pH ≤ 4.0. The new ternary mineral (quartz/goethite/kaolinite) CA-SCM with the addition of quartz component provides excellent predictions, suggesting quartz-sand adsorbs U(VI) more at pH near 3.0, kaolinite (exchange sites) contributes more at pH near 4.0, while goethite dominates at pH > 4.5. Potential influences of dissolved Al, Si and Fe on U(VI) adsorption are also discussed. This work is part of the Sustainable Systems Scientific Focus Area (SFA) program at LBNL, a project supported by the US Department of Energy for understanding and predicting long-term groundwater plume mobility and natural attenuation.

Characterization, Transformation, and Mobilization of Sediment-Associated Natural Organic Matter in Subsurface Sediments
Session/Location/Date/Time: Poster board in Session 25c, Tuesday @ 17:00 - 19:00

PATRICIA M. FOX*, RUTH M. TINNACHER, PETER S. NICO, BENJAMIN GILBERT, AND JAMES A. DAVIS
[1]Lawrence Berkeley National Lab, 1 Cyclotron Rd., Berkeley, CA 94720 (*corresponding auther email: pmfox@lbl.gov)

Abstract In this study, we investigated natural organic matter (NOM) associated with shallow alluvial aquifer sediments in a floodplain of the Colorado River in Rifle, Colorado, USA. Total organic carbon (TOC) contents in these subsurface sediments are typically around 0.1%, but can range from 0.03% up to approximately 1.0%. Total organic carbon content is largely correlated with sediment texture, which is highly heterogenous in this aquifer, with the highest TOC contents associated with naturally-reducing zones. Even at the typical TOC values of 0.1%, the sediment-associated OC is many times higher than the dissolved OC pool. The goal of this study was to better understand the exchange between the dissolved and sediment-bound OC pools under various biogeochemical conditions.

We have characterized the sediment-bound natural organic matter from several locations within the floodplain with differing physical and geochemical properties using a combination of *in situ* techniques, such as FTIR, and chemical extractions in order to determine the relative reactivity of the NOM and asssociations with mineral phases. Additionally, we have performed batch incubation experiments using both sterilized and un-sterilized sediments in order to characterize the release of NOM into the dissolved phase. Results from these experiments indicate that the reactive pool of NOM is limited to a small fraction of the total NOM, likely through chemical and physical protection mechanisms. During batch experiments, most of the OC is released to the dissolved phase during the first 24-hours, with very slow release thereafter. Further experiments will assess the effects of changing redox conditions on NOM release and transformation. Such fluctuating redox conditions may occur in a shallow aquifer such as this during the rise and fall of the water table associated with rainfall, snowmelt, and changing river stage, all of which may occur seasonally or with the onset of climate change.

Arsenic Chronospeciation in a Biostimulated Aquifer

Session/Location/Date/Time: Poster board in Session 20g, Thursday @ 17:00 - 19:00

HOBSON,C.[1], WILLIAMS, K.H.[1], STUCKER, V[2]. AND RANVILLE, J.[2]

[1]Lawrence Berkley National Laboratory, Berkley, CA
[2]Dept. of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO

Abstract The Deparment of Energy (DOE) monitors numerous former mill sites where bioremediation represents a potential approach for addressing groundwater contamination by uranium (U) and other aqueous metals. Bioremediation studies at DOE's Rifle, CO (USA) site have explored conversion of soluble U(VI) to insoluble U(IV) through organic carbon (acetate) addition, with work repeatedly demonstrating the ability to lower groundwater U concentrations through stimulation of iron and sulfate reducing bacteria. Ores milled at Rifle were enriched in numerous redox sensitive metals including arsenic (As), with ferric oxides present in sediments acting as strong sorbents for arsenate (As(V)). Pathways accompanying bioreduction of U can result in reductive dissolution of oxide sorbents and hence release of As(V) to groundwater.

Such As releases have been repeatedly observed at Rifle

during acetate injection, with the increases most pronounced when sulfate reduction is the primary form of metabolism. Although dissolution of sorbents is expected to account for some fraction of the increases, the close correspondence between elevated As and sulfidic conditions warranted analyis to assess the contribution of thiolated forms. To assess this possibility, speciation studies are being used to characterize As species present during various stages of the bioremediation process ('chronospeciation').

Using ion chromatography-inductively coupled plasma- mass spectrometry (IC-ICP-MS), As species are determined by comparison with retention times of prepared standards including arsenite, arsenate, mono-, di-, tri-, and tetra- thioarsenate. Groundwater samples obtained during sulfidic conditions when As concentration exhibited a 5-fold increase above pre-acetate injection values showed predominance of thioarsenic species, with di- and tri-thioarsenates the most abundant. The change in the coordination environment of the thiolated forms relative to those of arsenate or arsenite may explain the abrupt increase in groundwater As, as desorption from oxide surfaces is enhanced following exchange of As-O for As-S bonds occurs. Evaluation of U bioremediation success must therefore take into consideration the possibility of creating redox conditions favorable for the release of secondary contaminants.

Genome-to-Watershed Predictive Understanding of Terrestrial Biogeochemical Functioning: 'Sustainable Systems 2.0'
Session/Location/Date/Time: Poster board in Session 19a, Monday @ 17:00 - 19:00

SUSAN HUBBARD[1], DEB AGARWAL[1], JILLIAN F. BANFIELD[1,2], HARRY R. BELLER[1], EOIN BRODIE[1], PHILLIP E. LONG[1], PETER NICO[1], CARL STEEFEL[1], TETSU TOKUNAGA[1], KENNETH H. WILLIAMS[1]

[1]Lawrence Berkeley Natl. Laboratory, Berkeley CA 94720
[2]UC Berkeley, Berkeley CA 94720

Abstract Microbes in terrestrial environments regulate many vitally important processes, including mediating greenhouse gas fluxes and contaminant remediation. In spite of their critical role, little is known about complex interactions among microbes, minerals, migrating fluids and dissolved constituents that emerge in heterogeneous terrestrial environments across a great range of scales. The new, Department of Energy sponsored 'Sustainable Systems 2.0' project aims to develop a predictive understanding of how the subsurface microbiome affects biogeochemical watershed functioning, how watershed-scale processes affect microbial functioning, and how these interactions co-evolve with climate and land-use changes. The initial project investigations are being carried out at a Colorado River floodplain located in Rifle CO. This presentation will describe recent project advances: metagenomic analysis revealing the extraordinary genomic diversity of aquifer microbiomes and their roles in terrestrial system biogeochemical cycling; soil, vadose zone and groundwater biogeochemical monitoring revealing high spatiotemporal variability of DOC in response to hydrological pulses; approaches for quantifying organic-mineral associations; field redox manipulation responses; and progress in developing a genome-enabled watershed simulation capability.
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Modeling the Biogeochemical Response of a Flood Plain to Hydrologic Forcing
Session/Location/Date/Time: Poster board in Session 21b, Thursday @ 17:00 - 19:00

S. MOLINS, B. ARORA, N. SPYCHER, J.N. JOHNSON AND C.I. STEEFEL
[1] Earth Sciences Division, Lawrence Berkeley National Laboratory

Abstract The quantification of the carbon fluxes, stocks, and transformations in soils and watersheds is critical for closing key biogeochemical cycles and for developing predictive understanding of climate change scenarios. The Old Rifle site is located on the flood plain of the Colorado River. At present, site-wide field investigations focus on microbial metagenomic analyses, saturated and unsaturated zone hydrology and quantifying selected biogeochemical variables including organic carbon pools and inorganic carbon fluxes. Modeling is used to integrate these data and address the overarching goal of understanding of the impacts of climate and land use changes on the terrestrial ecosystem behavior.As component of the overall modeling approach, a 2-D Transect Infiltration model has been developed. The specific goal of this component is to capture the biogeochemical response of the Rifle Flood Plain subsurface system to hydrologic forcing, including snow melt, Colorado River stage, infiltration from Rifle uplands, and fluctuations in water table elevation.

As component of the overall modeling approach, a 2-D Transect Infiltration model has been developed. The specific goal of this component is to capture the biogeochemical response of the Rifle Flood Plain subsurface system to hydrologic forcing, including snow melt, Colorado River stage, infiltration from Rifle uplands, and fluctuations in water table elevation.

Simulation results are constrained by measurements of water and carbon fluxes, along with water table elevation, and by isotope and major element chemistry. Simulations are used to evaluate the relative contribution of flux from the unsaturated zone versus lateral groundwater flow and investigate how water table fluctuation affect processes maintaining sub-oxic conditions in the aquifer; in particular, how gas entrapment in the capillary fringe affects this sub-oxic condition.

The GEWaSC Framework: Multiscale Modeling of Coupled Biogeochemical, Microbiological, and Hydrological Processes (Invited)
Session/Location/Date/Time: 21b: Room 203, Friday @ 14:45 - 15:00

C.I. STEEFEL[1*], E.L. BRODIE[1], N. BOUSKILL[1], S. MOLINS[1], B. ARORA[1], S.B. YABUSAKI[2], U. KARAOZ[1], N. SPYCHER[1], R.M. MAXWELL[3], D. TREBOTICH[1], A. NAVARRE-SITCHLER[3], J. BEISMAN[3]
[1]Lawrence Berkeley National Laboratory, Berkeley, CA, CISteefel@lbl.gov (* presenting author)
[2]Pacific Northwest National Laboratory
[3]Colorado School of Mines

Abstract In order to improve our ability to predict the effect of climate change on carbon and nutrient cycling, we are developing a genome-enabled multiscale reactive transport framework (GEWaSC) that couples microbial composition, competition, and activity to biogeochemical processes and the hydrologic cycle at the watershed scale. The model will capture flow of water and flux of carbon and nutrients from the surface through the vadose zone and saturated zone, while simulating the dynamics of microbial community evolution and consequent changes in carbon and nutrient fluxes and aquifer biogeochemistry as a result of climate perturbations or other changes in the surface and subsurface environment.

This new simulation capability goes beyond conventional watershed models by ultimately integrating surface processes (e.g., those taking place in the soil and surface waters) with the subsurface flow and transport in a formal manner to provide a complete description of carbon, biogeochemical, and nutrient cycles within a catchment. A novel feature of the modeling approach is to couple microbial functional distributions inferred from trait-based models that are parameterized using site-specific 'omic data with a comprehensive simulation of biogeochemical networks. An important requirement of the framework is that it is capable of upscaling hydrologic, biogeochemical, and microbiological data from smaller to larger scales (up to the watershed scale), and in some cases downscaling processes and parameters to more focused, smaller scale simulations.

Initial model application is to biogeochemical and microbial dynamics within the Rifle Flood Plain system, a component of the greater Colorado River system. Scientific questions to be addressed include 1) What are the primary factors regulating redox status in aquifers and watersheds? 2) What are the effects of climate change influences, both gradual and abrupt relative to seasonal (baseline) variability, on carbon and nutrient cycling at the watershed scale?

Determining water and carbon fluxes into groundwater from a semiarid floodplain vadose zone

Session/Location/Date/Time: Session 20g ,Exhibit Hall D ,Thursday 12th June @14:00-14:15

TETSU K. TOKUNAGA[1*], JIAMIN WAN[1], WENMING DONG[1], KENNETH H. WILLIAMS[1], MARK J. ROBBINS[1], YONGMAN KIM[1], BORIS FAYBISHENKO[1], MARK E. CONRAD[1], JOHN N. CHRISTENSEN[1], CHAD HOBSON[1], BENJAMIN GILBERT[1], RICHARD D. DAYVAULT[2], PHILIP E. LONG[1], SUSAN S. HUBBARD[1]

[1] Lawrence Berkeley National Laboratory, Berkeley, CA 94720 USA (*correspondence: tktokunaga@lbl.gov)

[2]S.M. Stoller Corporation, Grand Junction, CO 94025 USA

Abstract Water and carbon fluxes from the vadose zone into groundwater need to be quantified to understand subsurface hydrobiogeochemical conditions and predict impacts of climate change. These fluxes are challenging to determine in semi-arid regions because of their low magnitudes. However, the remediated uranium/vanadium mill tailings site on the Rifle, Colorado floodpain possesses characteristics favorable for investigating subsurface transport, including locally derived fill soil with geochemical characteristics typical of the region, an established vegetation cover, geochemically distinct boundaries between the fill and underlying alluvium, predictable groundwater interaction with the adjacent Colorado River, and an impermeable lower boundary (shale at ~7 m depth). Within this well-defined hydrological system, we installed neutron probe access tubes and depth-distributed tensiometers, pore water samplers, and gas samplers along a transect aligned with the groundwater flow direction in order to determine inventories and fluxes of water, carbon, and other components. Seasonally dependent recharge into groundwater is quantified by combining field measurements with laboratory/pedotransfer constraints on hydraulic properties. High dissolved organic carbon (DOC) concentrations in the vadose zone (up to ~10 mM) relative to in groundwater (<1 mM), and increasing CO_2 concentrations with depth indicate the importance of deeper vadose zone OC transport and microbial activity. DOC characteristics and trends are being used to improve understanding of vadose zone fluxes of carbon into groundwater. Variations in carbon availability and water saturations at the capillary fringe are also reflected in changes to redox-dependent chemical components, including residual U and V. This effort is part of Sustainable Systems 2.0, a new Department of Energy project investigating climate-induced changes in subsurface carbon transport, biogeochemical transformations, and metabolic potential of microbial communities.

Carbon transport and transformation from vadose zone to groundwater

Session/Location/Date/Time: 20g , Exhibit Hall D ,Thursday 12th June @ 14:00-14:15

JIAMIN WAN[1]*, WENMING DONG[1], TETSU K. TOKUNAGA[1], KENNETH H. WILLIAMS[1], YONGMAN KIM[1], MARK E. CONRAD[1], BENJAMIN GILBERT[1], PHILIP E. LONG[1] AND SUSAN S. HUBBARD[1]

[1]Lawrence Berkeley National Laboratory, Berkeley, CA 94720
USA (*correspondence: jwan@lbl.gov)

Abstract The dynamics of carbon in the vadose zone, the interface between land surface and groundwater, are poorly understood yet important for predicting C cycling and responses to climate change. As a component within the LBNL Science Focus Area 2.0, this effort is designed to determine concentrations and speciation of C in vadose zone pore waters, how these characteristics differ from overlying soil and the underlying groundwater, and how transport and transformation rates for C in the vadose zone respond to changes in climate, vegetation, and microbial communities. Our initial investigations are at the Rifle Site along the Colorado River.

Within this floodplain, boreholes were drilled (down to 7 m depth) at three sites for sediment sampling, and instrumented with pore water and gas samplers at 0.5 to 1 m intervals in the vadose zone and aquifer, and with thermistors at generally wider intervals. Vadose zone pore waters, groundwaters, and vadose zone gas samples have now been collected periodically for ~1 year. Analyses include DOC, DIC, major and trace elements, and δ13C of the DOC and CO2 gas samples. Different collection methods and analyses are enabling seasonally and vertically resolved geochemical profiles of the vadose zone pore-waters. We found that DOC concentrations are many times higher in the vadose zone than in groundwater, and vary seasonally in the vadose zone and capillary fringe, but the groundwater. The decreased aromaticity of DOC in the pore waters with greater depth, the identified DOC speciations, and δ13C isotope data all suggest complex biogeochemical transformations during transport through dynamic vadose zone gradients of moisture and temperature. Quantitative understanding of C, O, N, and potentially microorganisms cyclically transported from the vadose zone into groundwater are important for understanding the system response to climate and hydrologic changes, and the Rifle site studies will provide key data that will help us unravel those responses.

A floodplain perspective on elemental cycling and uranium plume persistence (Keynote)

Session/Location/Date/Time: Session 20g , Exhibit Hall D ,Thursday 12th June @14:00 - 17:00

KENNETH H. WILLIAMS[1]*, JOHN R. BARGAR[2] AND THE RIFLE SCIENCE TEAM[1]
Lawrence Berkeley National Laboratory, Berkeley, CA
94720 USA (*correspondence: khwilliams@lbl.gov) 2
Stanford Synchrotron Radiation Lightsource, Menlo Park, CA 94025 USA

Abstract Experiments at the Department of Energy's Rifle, CO (USA) field site have long focused on stimulated biogeochemical pathways arising from organic carbon injection. Although reductive pathways and their relation to uranium (U) immobilization have been a focus since 2002, ongoing studies are exploring oxidative pathways and their role in mediating fluxes of C, N, S, and aqueous metals. Insights gained from such 'stimulation' experiments are providing insight into analogous natural biogeochemical pathways that mediate elemental cycling in the absence of exogenous carbon. Such reactions are instead mediated by endogenous pools of natural organic matter (NOM) deposited during aggradation of aquifer sediments associated with fluvial processes within the Colorado River floodplain.

Discrete lenses of fine-grained, organic-rich sediments (up to 2% organic C and N) enriched in reduced species, such as Fe(II), iron sulfides and U(IV) have been identified along the active margin of the floodplain. Referred to as "naturally reduced zones" (NRZs), these localities constitute a distinct facies type (i.e., 'biogeofacies') within an otherwise gravel- dominated, largely NOM-deficient matrix. NRZs contain

100-fold higher U concentrations than surrounding aquifer sediments and represent 'hotspots' of seasonally intense C, N, S, and U cycling during excursions in groundwater elevation. Imbibition of air bubbles within the capillary fringe is inferred to contribute to seasonally oxic groundwater, with its impact on redox-mediated reactions exhibiting close correspondence to those induced through the intentional introduction of oxidants. Reactions induce sharp gradients in nitrate and sulfate resulting from elevated rates of nitrification and oxidation of reduced sulfur as dissolved oxygen becomes non-limiting. 7-fold increases in aqueous U are observed during this period likely contributing to U plume persistence.

Because NRZs contain large stores of NOM and have an outsized capacity to mediate redox transformations of relevance to U mobility, they are expected to exert influence over the redox status and biogeochemistry of contaminated floodplain deposits worldwide, with major implications for long-term contaminant bioavailability.

2.0 SFA 2.0 COLLABORATOR ABSTRACTS

Bioremediation to plume persistence: Uranium biogeochemistry in naturally and artificially bioreduced aquifer sediments
Session/Location/Date/Time: 10d: Room 304, Tuesday @ 14:30 - 14:45

J.R. Bargar[1,*], N. Janot[1], D.S. Alessi[3], M.E. Jones[1], K.H. Williams[2], P.E. Long[2], R. Bernier-Latmani[3], and J.M. Cerrato[4]
[1] Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA (*correspondance: bargar@slac.stanford.edu)
[2] Lawrence Berkeley National Laboratory, Berkeley, CA 94720 USA
[3] École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
[4] University of Alberta, Edmonton, Alberta, T6G 2E3, Canada.
[5] University of New Mexico, Albuquerque, NM, USA

Abstract Manipulating the subsurface redox status of uranium has been proposed as an *in-situ* bioremediation strategy. Recent evidence suggests that biologically driven redox reactions in organic-rich sediments play major roles in maintaining uranium groundwater plumes in the upper Colorado River basin (U.S.A.). The speciation of uranium in these systems is poorly constrained but critical to predicting uranium fate and transport. Moreover, it is necessary to understand how biogeochemical cycles of other elements, including C, N, Fe, and S couple to those of uranium.

The SLAC SFA program has investigated reduced uranium, carbon, sulfur, and iron species at molecular to pore scales *in-situ* in the biostimulated aquifer and in sediments from organic-rich naturally-reduced zones (NRZs) at the U.S. Department of Enery's Rifle, CO field site. The purposes of this work are to constrain uranium speciation, understand the coupling of C, N, Fe, S and U redox cycles, and to characterize biogeochemical interactions between NRZs and the surrounding aquifer.

This talk will compare and contrast artificially and naturally bioreduced sediment systems. The rate and extent of uranium reduction appears to be closely tied to sulfur reduction. A coupled biological-abiotic process model will be discussed to account for the relative abundance of non-crystalline forms of U(IV) in both systems. It will be shown that aquifer-NRZ interfaces are biogeochemical hot spots that likely facilitate uranium resupply to aquifers.

Effect of groundwater solutes on uraninite stability: laboratory and field studies
Session/Location/Date/Time: 10d: Room 304, Tuesday @ 14:45 - 15:00

J.M. CERRATO[1]*, J. LEZAMA-PACHECO[2], K.H. WILLIAMS[3], P.E. LONG3, D.S. ALESSI[4], E. SUVOROVA[5], R. BERNIER-LATMANI[5], D.E. GIAMMAR[6] AND J.R. BARGAR[7].
[1]University of New Mexico, Albuquerque, NM, USA
jcerrato@unm.edu (* presenting author)
[2]Stantord University, Palo Alto, CA, USA
[3]LBNL, Berkeley, CA, USA
[4]University of Alberta, Edmonton, AB, Canada
[5]École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland
[6]Washington University, St. Louis, MO, USA
[7]Synchrotron Radiation Lightsource, SLAC, Menlo Park, CA, USA,

Abstract *In-situ* bioremediation strategies target the immobilization of uranium in contaminated sites by stimulating microbial reduction of U(VI) to less soluble U(IV). Biogenic uraninite and U(IV) bound to biomass are among the resulting products of U(VI) bioreduction. Uraninite is the preferred form of U(IV) for *in-situ* bioremediation as it is less soluble than other U(VI) and U(IV) species. Understanding the effect of groundwater solutes on uraninite stability in reduced sediments is crucial for the success of bioremediation strategies.

We performed laboratory and field studies to investigate the effect of groundwater solutes on uraninite dissolution by integrating aqueous chemistry and solid characterization methods. Uraninite dissolution under anoxic and oxic conditions with an influent solution containing dissolved inorganic carbon was lower in the presence of Ca than in de- ionized water. X-ray absorption spectroscopy (XAS) and solution chemistry analyses suggest that adsorbed or precipitated Ca2+ phases may inhibit oxidative uraninite dissolution.

We performed field experiments in oxic and anoxic wells

at the Old Rifle, CO site to better understand the oxidative dissolution of uraninite over 650 days. By placing biogenic uraninite in tubes covered with a membrane that allowed diffusive exchange and placing the tubes in the aquifer (~ 10 mM inorganic carbon), uranium loss could be quantified. After 102 days, around 50% uranium loss was observed from the tubes deployed under oxic conditions. However, only less than 3% loss was observed from the anoxic well. After 650 days, 65% and 85% loss was observed under oxic conditions whereas the corresponding U loss in the anoxic control remained negligible. Ca K-edge EXAFS linear combination

and shell by shell fits suggest that: a) Ca2+ adsorbed to the

surface of uraninite; and b) it is possible that a U-Ca-O phase formed a thin layer on the surface of reacted biogenic uraninite. Our results suggest that Ca and other groundwater solutes increase the long-term stability of uraninite in subsurface environments.

Assessing the potential of geophysical methods to detect subsurface changes in iron-mineral chemistry

Session/Location/Date/Time: Poster board in Session 10e, Tuesday @ 17:00 - 19:00

C. ROSIER[1], K. KEATING1, K. WILLIAMS[2],D. NTARLAGIANNIS[1], E. GRUNEWALD[3] AND D. WALSH[3]

[1]Rutgers University, Newark, NJ 07102, USA (*correspondence: carl.rosier@rutgers.edu, kmkeat@andromeda.rutgers.edu, dimntar@rutgers.edu)
[2]Lawrence Berkeley National Lab, Berkeley, CA 94720, USA (khwilliams@lbl.gov)
[3]Vista Clara, Inc. Mukilteo, WA 98275, USA (davewalsh@vista-clara.com, elliot@vista-clara.com)

Abstract In this study the geophysical methods nuclear magnetic resonance (NMR), spectral induced polarization (SIP), and magnetic susceptibility (MS) were examined to determine the sensitivity of each method to monitor *in situ* iron redox processes within natural sediments. Laboratory column and field experiment were conducted using sediments and infrastructure from the Rifle Intergrated Field Research Challenge site (IFRC), 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.

Laboratory measurements were collected on columns packed with Rifle sediments and amended with acetate intended to stimulate microbial reduction. Laboratory results indicate limited change in NMR relaxation time values and a slight decrease in the MS values after amendment, suggesting that the magnetic mineral magnetite was not produced. SIP values increased within the amended columns corresponding to the expected formation of iron sulfide minerals.

Continuous borehole measurements were collected using the NMR Javelin logging tool developed by Vista Clara. Measurements were collected in previously amended sediments during spring runoff, at which time oxidation of the sediments was expected due to increases in dissolved oxygen. Following runoff, injection of acetate into aquifer sediments occurred designed to mimic the laboratory biostimulation experiment. The results from the field study indicate that borehole NMR measurements are capable of detecting changes in iron geochemistry as a result of the oxidation of previously amended sediments. However, the subsequent addition of acetate failed to alter the NMR signal suggesting exhaustion of the bioavailable iron pool.

238U/235U changes in groundwater associated with re-oxidation of reductively immobilized uranium

Session/Location/Date/Time: Poster board in Session 20c, Tuesday @ 17:00 - 19:00

A. E. SHIEL[1]*, C. C. LUNDSTROM[1], T. M. JOHNSON1, P. E. LONG[2] AND K. H. WILLIAMS[2]

[1]Dept. of Geology, University of Illinois at Urbana- Champaign, Urbana, USA;
*ashiel@illinois.edu
2Lawrence Berkeley National Laboratory, Berkeley, USA

Abstract Uranium is soluble, relatively mobile and toxic in its oxidized state, U(VI). In contrast, U is relatively insoluble and generally immobile in its reduced state, U(IV). This has led to the pursuit of U(VI) reduction as a remedial strategy for contaminated groundwater. Both laboratory and field studies have revealed that the rate of 238U removal is slightly higher than that of 235U for microbial U(VI) reduction (discussed as δ238U). At the former U mill site in Rifle, CO (USA), acetate- induced biostimulation (under both iron and sulfate reducing conditions) results in shifts in the δ238U of U(VI) of −1.3 and −1.9‰, respectively, for a >90% apparent U(VI) loss. These changes in 238U/235U accompany large changes in U concentration (dropping from 150–200 ppb U to ~10 ppb U) and demonstrate the use of 238U/235U to detect and quantify the extent of U(VI) reduction in groundwater.

Uranium is readily oxidized by dissolved oxygen (DO) and other oxidants, such as nitrate, MnO2, and ferrihydrite, posing a problem for long-term bioremediation efficacy. Because reduction of U(VI) deposits isotopically heavy U(IV) toward the upgradient side of the reduction zone, remobilization of this U has the potential to reveal itself in the form of isotopically heavy dissolved U(VI) should oxidation accompany the cessation of active remediation and a rebound in aquifer redox status.

To examine changes in U concentration and 238U/235U accompanying re-oxidation, we present results of two field experiments (2012 and 2013) performed at the Rifle site. In both experiments, an oxidant (DO and nitrate, respectively) was injected into a previously biostimulated plot (2011 and 2012). Both DO and nitrate injections led to U concentration increases (up to 270 and 550 ppb, respectively), well above that of upgradient groundwater (~175 ppb). For the DO injection, U concentration increases were accompanied by increasing δ238U from −0.60‰ to 0.00‰, possibly indicative of re-oxidation of isotopically heavy U(IV). δ238U results from the nitrate injection will provide additional clarification.

This study provides the first examination of U isotope systematics during re-oxidation in the field and thus contributes to the development of 238U/235U as a valuable tool for assessing U bioremediation efforts.