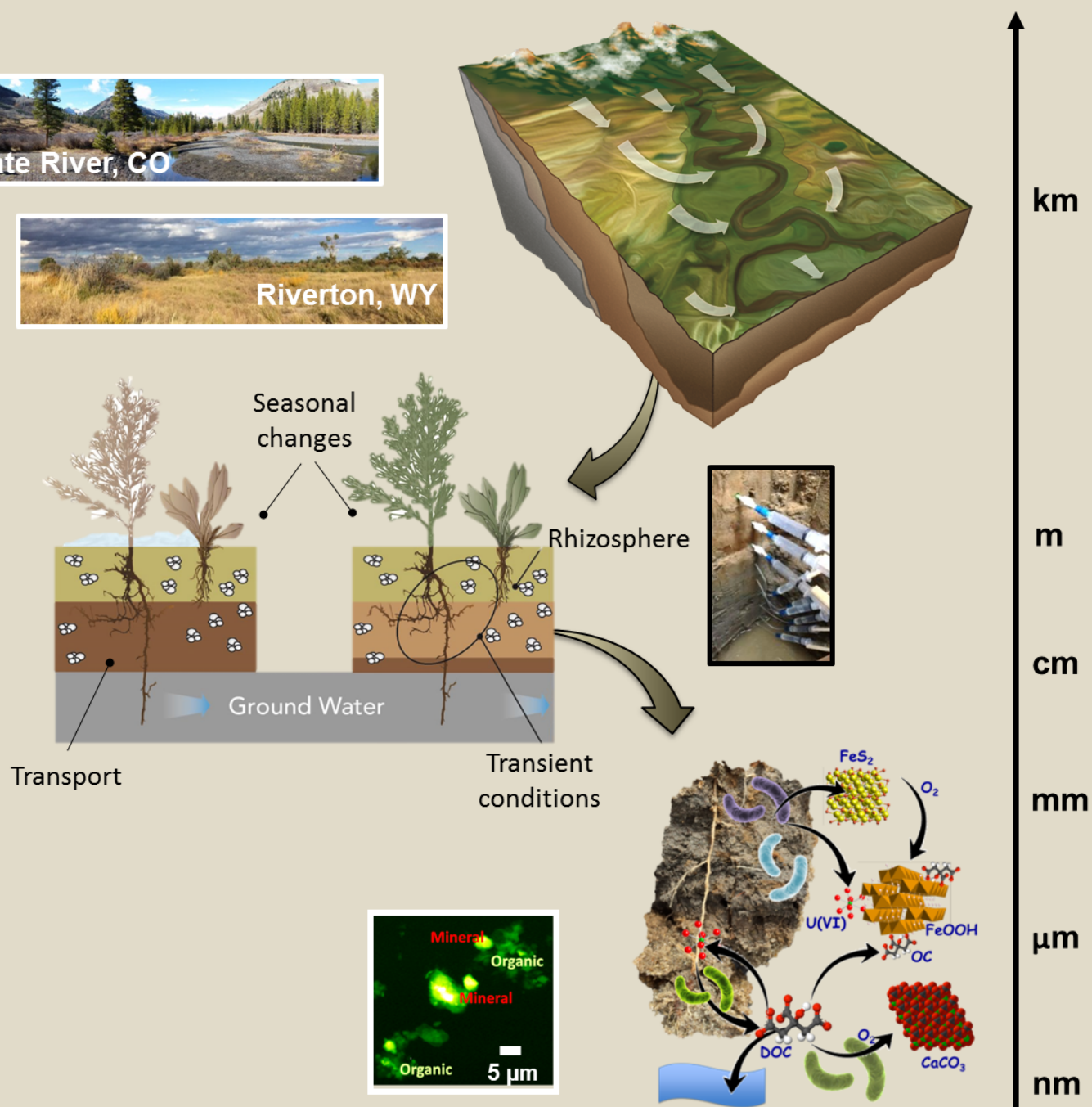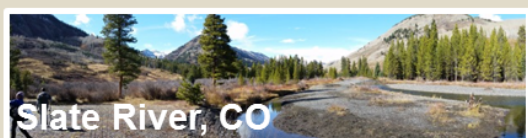# SLAC SFA

Hydrologically driven biogeochemical processes controlling groundwater quality

2018 ANNUAL REPORT

June 30, 2018

John R. Bargar, Principal Investigator and Project Manager
Stanford Synchrotron Radiation Lightsource,
a Directorate of SLAC

Co-principal investigators:
Kristin Boye (SSRL), Scott Fendorf,
Chris Francis, and Kate Maher (Stanford University)

June 30, 2018

Highlights

Hydro-biogeochemical activity profoundly influences groundwater quality across the Western U.S. Spring flooding and high groundwater conditions followed by summer drought produce intense, cyclic reducing-oxidizing transitions that trigger changes in microbial metabolic activity, dissolution and reprecipitation of solids, transformations of iron, sulfur, uranium and metals, and release/uptake of carbon and contaminants. While these processes are important to watershed modeling efforts nationwide, *we lack a robust predictive understanding of when thresholds for redox transformations are reached in relation to soil moisture, metabolic responses, and rates and connection nodes of reactions, and how they control groundwater quality.*

In the new CESD Strategic Plan, BER has emphasized the need for advancing our understanding of how repeated perturbations and geochemical-genomic-metabolic interactions impact the biogeochemical function of Earth systems; prediction of future environmental states under perturbation; and sustenance and threshold conditions for biogeochemical hot spots. The Groundwater quality SFA program is helping to advance these goals by investigating the coupling of hydrological and biogeochemical processes in alluvial floodplain sediments and how they impact groundwater quality. We are studying how hydrological-biogeochemical interactions create and sustain thermodynamic disequilibrium ("hot spots/moments"), the triggers and thresholds for these conditions, how we can represent these systems in quantitative model frameworks, and how they impact groundwater quality. Because hydro-biogeochemical compartments (soils, capillary fringe, saturated zone) are strongly coupled in alluvial systems, we have structured the project into four subtasks, each linking hydrology to biogeochemistry and water quality through process and numerical modeling in: 1) the rhizosphere, 2) transiently reduced zones, 3) the shallow aquifer, and 4) contaminant-hosting phases.

Since our last update (in the triennial proposal, Mar 2017), we have published 18 manuscripts (accepted or published), submitted another 3 manuscripts (in review), and presented 18 talks (3 keynotes, 7 invited) and 13 posters at scientific meetings. Key accomplishments during the review period include:
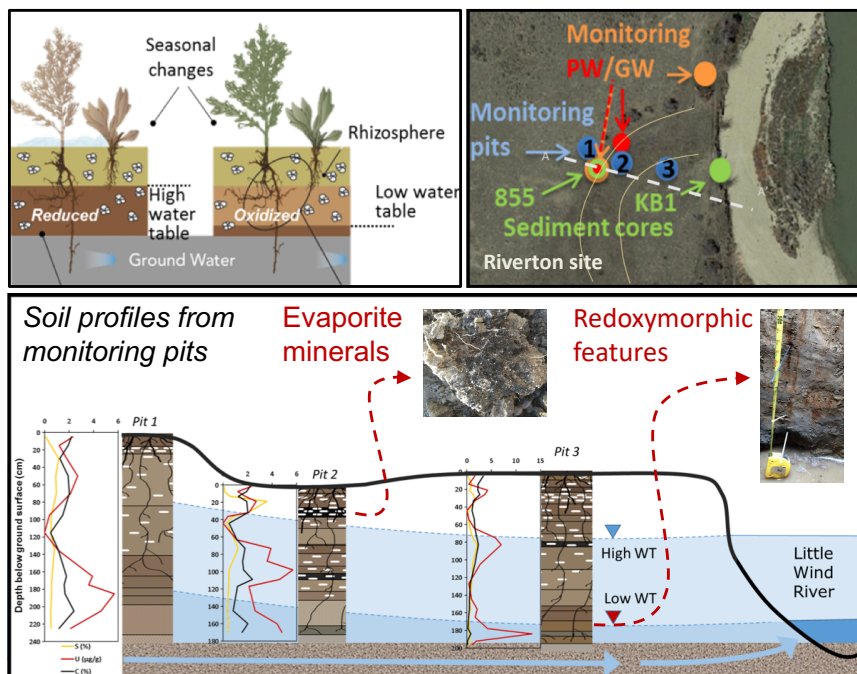
1. **Demonstrated that non-crystalline U(IV) is the dominant reduced U species in naturally reduced zones (NRZs) across the upper Colorado River Basin**[1,7] (superscripts 1-21 refer to our publications, *cf.,* Appendix A). Uranium in this form can accumulate in waterlogged sediments, but is highly sensitive to oxidation and re-mobilization when water tables drop and air re-enters pore spaces. This tendency to switch between immobile and mobile forms in response to hydrologic triggers contributes to plume persistence in the upper CRB.

2. **Discovery that wet-dry cycling stabilizes U as crystalline U(VI) in fine-grained organic-enriched capillary fringe alluvium**[1]. This finding shows that hydro-biogeochemical redox cycling stabilizes U in shallow sediments via *multiple* distinct mechanisms and in multiple oxidation states. Such strong sediment-uranium interactions further help to explain why uranium plumes are long lived in the upper CRB.

3. **Discovery of vertical transport as a major process controlling seasonal U biogeochemistry and mobility in semi-arid alluvial environments** (Roycroft *et al.,* in prep.). We have found that U is readily transported down *and up* between shallow soils and underlying TRZs in response to inundation (rain/flooding) and evapotranspiration (capillary rise). U mobility is facilitated by prevalent shallow adsorbed U(VI), rapid onset of transient

reducing conditions, rapid reductive U(IV) trapping, and rapid oxidation of U(IV) when oxygen re-enters TRZs. We expect that other solutes exhibit robust up-down transport, providing a mechanism to couple biogeochemical processes in vertically differentiated zones.

4. **Generated a microbial community database using deep 16S rRNA gene sequencing that is unprecedented in its size and regional extent (160 samples, 20 million reads, 5 sites covering 700 km) and focus on vertical profiling across the soil-groundwater interface** (Cardarelli *et al.,* in prep.). This framework illuminates the distribution of microbial-geochemical processes

Figure 1. **Top left:** Conceptual cross-section of an alluvial floodplain showing major vertically-resolved compartments: soil, capillary fringe, and aquifer. In spring, infiltration and water table rise favor reducing conditions. In summer, the capillary fringe drains, leading to oxidizing conditions. At the same time, evapotranspiration drives upward solute transport, resulting in evaporite mineral formation. **Top right:** Riverton, WY, field site by Little Wind River. Pits were dug at locations 1, 2, and 3. **Bottom**: schematic of soil profiles and U (red), C (black), and S (yellow) concentrations with depth in a transect corresponding to dashed line in top right.

across hydrologic zones in shallow alluvium, and allows microbial community comparisons within a soil profile, across a site, and between sites.

5. **Generated comprehensive seasonal biogeochemical datasets for porewater and sediments in the variably saturated (transiently reduced) zone at the Riverton field site.** (Bobb *et al.* in prep.; Boye *et al.* in prep). Detailed depth- and time-resolved porewater and sediment samples were collected from snowmelt (April) through flood (June), dry season (July- Sept) and fall wet-up (Oct-Nov). This unique dataset is a significant achievement and provides the basis for model development, metagenome mining, scientific discovery, future sampling, and multiple manuscripts.

6. **Applied microbial energetics to understand redox transformations in saturated soils and sediments**[2,5] This work shows that applying thermodynamic theory to constrain microbial C oxidation while tracking mass and energy balances during redox transformations is a promising avenue for predicting outcomes of biogeochemical processes in heterogeneous systems with various active microbial metabolic strategies and complex substrates.

1. Program overview

Few terrestrial environments are more emblematic of, and influenced by, redox transitions than alluvial floodplains, where seasonal and episodic drought and flooding produce strong anoxia/ oxia oscillations (**Fig. 1**). This hydro-biogeochemical activity profoundly influences groundwater

quality across the Western U.S. and, due to the considerable contribution of groundwater discharge to stream and river water runoff, also impact downstream surface water quality. We know in general that redox transitions are triggered by changes in water saturation and moderated by sediment properties that regulate oxygen supply and demand, such as organic matter concentration and sediment texture[6]. The corresponding microbial metabolic activity transforms carbon, nutrients, minerals, and contaminants and alters their susceptibility to transport[1,2,5,7]. Crucially, however, **we lack a robust predictive understanding of when thresholds for redox transformations are reached in relation to soil moisture, metabolic responses, and rates and connection nodes of reactions**. This gap reflects an underlying deficiency in our detailed conceptual knowledge of biogeochemical reaction networks that govern redox transitions in the capillary fringe and transiently saturated zones. The resulting uncertainty prevents us from accurately capturing these systems in numerical models. Yet, redox transitions are profoundly important to watershed modeling efforts nationwide. Further, our knowledge is limited regarding solid phase hosts for contaminants, as well as contaminant mobilization/ immobilization mechanisms during redox transitions. Without such knowledge, we cannot link retention/ release behavior of contaminants to biogeochemical, redox, and water cycles, *i.e.*, necessary to accurately represent contaminant mobility in reactive transport models.

The mission of the SLAC SFA is to address the overarching question: *How do biogeochemical and transport processes in alluvial groundwater systems (bedrock to soil) couple to one-another and mediate water quality under hydrologically variable conditions?* We are performing research to (i) **experimentally interrogate** and (ii) **model** process couplings in shallow alluvial systems impacted by mining and ore processing activities.

Approach: We are combining field measurements with laboratory experiments and fine-scale (molecular to mm level) investigations of the interactions between hydrology, sediment properties, microbiology, and plant roots. Through integrated efforts between team members, approaches, and subtasks, we are striving to generate a holistic understanding of the coupled hydrological and biogeochemical functioning of alluvial systems, with the Riverton, WY, floodplain as our main research site. In addition to publishing our findings in peer reviewed journals, we will produce process representations and improved reaction networks for incorporation with existing and new reactive transport models. Hence, we will advance both the conceptual understanding and our ability to accurately represent these systems in modeling frameworks, which will advance our predictive understanding of hydrological perturbations on groundwater quality in shallow alluvial aquifers.

Importance of synchrotron techniques. Synchrotron x-ray absorption spectroscopy (XAS) provides unique capabilities to study molecular and electronic structure around nutrients and contaminants in complex, dilute natural materials. Synchrotron x-ray microscopy allows biogeochemical reactions to be imaged in 2D and 3D at spatial resolutions down to 30 nm. These techniques are crucial to providing molecular perspectives to support process knowledge at pore to regional scales.

Importance of external collaborations. Biogeochemistry is a highly diverse and complex field, with many disciplines involved and techniques to be mastered. To gain knowledge and experimental expertise that complement our strengths, we are collaborating with external groups through cooperative arrangements and scientific user facility proposals (*cf.* section 4.d.). These interactions provide access to expertise regarding, *e.g.*, ultra-high resolution mass spectrometry and isotope nano-imaging (M. Tfaily and J. Cliff, EMSL), microbe-mediated trace gas flux

analysis (L. Meredith, U. Arizona), Zn inorganic geochemistry (G. Morin, Sorbonne Université), and colloid transport in unsaturated soils (J.-P. Gustafsson, Swedish University Agricultural Sciences). Our collaborative publications (Appendix A) reflect this activity.

Impact and relevance to BER: Experiments and observations conducted by this program will provide needed molecular-, process-, and field-scale data required to constrain and develop new and more accurate biogeochemical models. Quantitative process representations and reaction networks produced by this project will help to advance BER toward its Biogeochemistry Scientific Grand Challenge goals[31], with strong contributions to understanding the impact of repeated perturbations and geochemical-genomic-metabolic interactions on the biogeochemical function of Earth systems; prediction of future environmental states under perturbation; and sustenance and threshold conditions for biogeochemical hot spots.

2. Outline of scientific objectives

This project is focused on understanding the coupling of hydrological and biogeochemical processes in alluvial floodplain sediments and how they impact groundwater quality. To gain a holistic understanding of these systems, we are focusing on four subtasks, each linking hydrology to biogeochemistry and water quality through process and numerical modeling: 1) the rhizosphere, 2) transiently reduced zones, 3) groundwater, and 4) contaminant-hosting phases.

Subtask 1. Influence of rhizosphere processes on carbon dynamics and contaminant hosting solid phases. *Knowledge gap: Little is known about the quantitative influence of roots on biogeochemical processes impacting contaminant mobility over spatial scales ranging from molecular-to-field and temporal scales from minutes-to-years.* Plants drive evapotranspiration with direct impact on the precipitation of evaporite minerals. Microbial activity and respiration is typically higher around roots than in bulk soil, which accelerates oxygen consumption and the onset of reducing conditions. Roots also contribute considerably to soil organic matter input through exudates and sheathed/senescing root biomass. The governing hypothesis for this subtask is that root presence modifies the organic matter composition and the rate of precipitation/dissolution, abundance, and type of minerals that form in response to hydrological changes, thereby impacting which solid and mobile phases are available for hosting contaminants. Rhizobox experiments and field investigations are combined to test this.

Subtask 2. Biogeochemical redox responses to hydrological transitions. *Knowledge gap: Our ability to accurately model redox transitions in the capillary fringe and predict their impact on water quality is nascent.* This subtask targets: (i) identification of key microbial functional guilds and understanding of their metabolic activity in relation to hydrologically impacted geochemical conditions, (ii) detailed knowledge of key thresholds and environmental triggers of biotic and abiotic reactions, and (iii) defining conceptual and numerical reaction networks that accurately connect organic matter to microbial metabolism and resulting geochemical transformations in response to hydrological changes. We are combining field observations with repeated single-variable manipulations in lab incubations and flow reactor experiments. Through detailed investigations with advanced microbiological 'omics' probing and geochemical techniques, we aim to decipher the key thresholds, triggers, and reaction nodes that are critically needed to drive biogeochemical reaction models in variably saturated sediments.

Subtask 3. Impact of hydrological-biogeochemical coupling on solute transport and groundwater biogeochemistry. *Knowledge gap: How are biogeochemical processes in shallow aquifers coupled to and mediated by overlying capillary fringe and soil processes?* This subtask

aims to assess the impact of vertical solute import (from overlying soil and sediments) on groundwater chemistry in relation to the influence of solute exchange between groundwater and reduced sediment porewater (diffusion controlled). Due to the presence of high biogeochemical activity in the capillary fringe and a strong vertical exchange, we posit that the aquifer system has a threshold response, whereby hydrologic coupling with the overlying sediments drives water quality in the underlying aquifer. We are testing this through a series of column experiments combined with field observations.

Subtask 4. Mechanisms controlling release/uptake of nutrients and contaminants. *Knowledge gap: It is not known which chemical species and mechanisms are responsible for stabilization and mobilization of contaminants and nutrients during redox oscillations and due to ET-driven upward transport in hydrologically dynamic alluvial systems.* Several hypotheses are driving the work within this subtask (Table 1), with the joint goal of deciphering the molecular level association of contaminants (U, Mo, Pb, Zn) with solid and mobile phases in various redox conditions and different hydrological stages. We are using a suite of advanced molecular level methods, including synchrotron X-ray techniques and high-resolution mass spectrometry, to examine solid phase and colloidal samples from natural and laboratory model systems.

By experimentally interrogating process linkages within and between the major compartments in shallow alluvial systems, we are developing an unprecedented system-scale understanding of water quality controls and dynamics. By integrating this knowledge into conceptual and numerical process representations, we are reducing model uncertainty while simultaneously advancing our ability to predict impacts of hydrological perturbations on groundwater quality.

3. National Laboratory program and management structure

Organizational structure. The SLAC SFA program resides within the Chemistry and Catalysis division at the Stanford Synchrotron Radiation Lightsource (SSRL), a Directorate of SLAC. The lead PI and technical research manager, John Bargar, reports to the SSRL Science Director and head of the Chemistry and Catalysis Division, Britt Hedman. Oversight and management decisions regarding the SLAC-SFA are made by Bargar, the Co-PI team, and Hedman.

Relationship with SSRL. SSRL is a DOE Office of Science user facility dedicated to structure-function characterization of materials, chemical, and biological systems. Being directly within the SSRL organization provides the Groundwater Quality SFA program with the most intimate possible contact with cutting-edge methodological developments and expertise. The Groundwater Quality SFA program contributes to SSRL strategic planning and beam station capabilities, and these developments in turn help to optimize beam lines for biogeochemistry research needs. SFA researchers help provide advice for experiment planning, execution, and data analysis to visiting BER-funded scientists (total effort level less < 5%).

Relationship with BER-funded structural molecular biology (SMB) program. The SMB program directly and indirectly helps the Groundwater Quality SFA researchers through its support for X-ray absorption spectroscopy and microXAS imaging staff, instrumentation, and operations.

Relationship with Stanford University. SLAC has a relationship to Stanford analogous to that of a school within the University. The Groundwater Quality SFA benefits tremendously from this proximity to Stanford. It helps us to attract the best and brightest students and postdoctoral researchers from around the globe. We have access to world-leading expertise in geochemistry, soil science, hydrology, numerical modeling, and environmental molecular microbiology. We

also have access to research facilities available on the Stanford campus, including the School of Earth Sciences Environmental Measurement laboratory, which has analytic capabilities for soil, water, and gas quantification, and Stanford nano-shared facilities, which houses cutting edge characterization and laboratory facilities and expert staff.

Communications. The cornerstone of our communications is the weekly meeting, where we communicate ongoing research results, discuss important recent literature, plan research and manuscripts, evaluate progress towards goals, and adjust the group effort to maintain focus on key priorities. To help ensure robust participation by students and postdoctoral researchers, the weekly meeting is coordinated by postdoctoral researchers.

Mentoring tomorrow's scientific workforce. We expect and encourage post-doctorals and students to develop strong communication, mentoring, and networking skills, necessary to become strong independent scientists. Our professional development program emphasizes: publishing papers, presenting results at scientific meetings, organizing symposia, writing proposals, reviewing proposals, and participating in field work and modeling activities.

4. Performance milestones and metrics toward accomplishing objectives

A major effort for the SLAC SFA program in FY2018 has been to initiate the new science plan approved in September 2017. Success in our project milestones requires early success in the field. Therefore, we have focused on analyzing samples and data collected from the Riverton site during summer-fall 2017 and strategically ramping up new sampling activities at the Slate River site. To support sample analyses, we submitted proposals to the Joint Genome Institute (JGI) – Environmental Molecular Sciences Laboratory (EMSL) joint FICUS research program, and to synchrotron user facilities (SSRL and CLS). Activities are under way for all subtasks in the new scientific program, except for subtask 1, which is scheduled to begin in FY2019. Several manuscripts are being prepared from existing field data.

Table 1. Summary of FY2017-2018 program and goals for FY2019. Grey text corresponds to subtasks which were not scheduled to be active in FY2018.

Hypotheses	FY18 goal	Status	Pages in report	Deliverables
Subtask 1. Influence of rhizosphere processes on carbon dynamics and contaminant-hosting phases				
Hypothesis 1.1. Root presence increases the rate of formation and abundance of mineral precipitates in capillary fringe conditions				
1.1.a. Roots increase evaporite mineral precipitates	Starting FY19	NA	NA	NA
1.1.b. Roots modify types of evaporite mineral precipitates	Starting FY19	NA	NA	NA
Hypothesis 1.2. Roots modify the types of minerals that form in response to changing water saturation				
	Starting FY21			
Hypothesis 1.3. Export of plant derived C from the rhizosphere is dominated by CO_2 and dissolved inorganic C; Decomposition products from soil organic matter and colloids dominate the export of organic C				
1.3.a. Plant derived C exported from rhizosphere is dominantly inorganic	Starting FY20	NA	NA	NA
1.3.b. Organic C export from rhizosphere is dominantly from SOM	Starting FY20	NA	NA	NA
Subtask 2. Biogeochemical redox responses to hydrological transitions				
Modeling task 2.1. Modeling of thresholds that determine onset and development of reducing conditions in TRZs using fine-scale reactive transport (10s of mm) under steady-state conditions	• Field sampling • Setup model framework	In progress	8-9	• This report • PI meeting posters

|				
Modeling Task 2.2. Reaction network modeling of TRZ sediment Fe/S redox cycles.	• Field sampling • Setup model framework	In progress	8-9	• This report • PI meeting posters
Hypothesis 2.3 TRZ sediments will exhibit large-scale shifts in dominant functional guilds corresponding to oxic (unsaturated) vs. reducing (saturated) conditions				
2.3.a. Nitrifiers will be most abundant and active under oxic conditions, dropping off rapidly as conditions become anoxic and especially sulfidic.	• Field sampling	In progress	10-12	Manuscript in prep. (Cardarelli) This report
2.3.b In the presence of trace sulfide, nitrate-reducing communities will be partially inhibited by Mo limitation.	Starting FY19	NA	NA	NA
Subtask 3. Impacts of hydrological-biogeochemical coupling for solute transport and groundwater biogeochemistry				
3.1 NRZs dominate contaminant sequestration and nutrient release to GW during the dry season and when infiltration is limited	• Conduct column experiments	In progress		
3.2 Infiltration associated with rain events delivers microbially available organic carbon and nutrients from overlying soils/sediments, stimulating biogeochemical cycling in the shallowest portion of the aquifer	Starting FY19	NA	NA	NA
3.3 Rapid snow melt of floodwater infiltration leads to oxidative release and evaporate dissolution, releasing salts and contaminants and impacting the entire aquifer	• Analyze data • Write manuscripts	In progress	12	NA
Modeling Task 3.4. Reactive transport modeling advective coupling of TRZs and underlying saturated zone	Starting FY19	NA	NA	NA
Subtask 4. Mobilization of U, Mo, Zn, Pb under hydrologic perturbation				
Hypothesis 4.1. Inorganics: dissolution of goethite during onset of reducing conditions mobilizes Pb(II) and Zn(II), and creates conditions conducive to colloid formation				
4.1.1.a Pb(II) is stored and released from internal lattice sites and surface sites in/on mackinawite and goethite	Starting FY20	NA	NA	NA
4.1.1.b Zn (II) is stored and released from internal lattice sites and surface sites in/on mackinawite and goethite	Starting FY20	NA	NA	NA
4.1.2 Inorganic sulfide colloids are produced during onset of reducing conditions	• Conduct batch experiments	In progress		• This report • Manuscript 3 (Appendix A)
Hypothesis 4.2. Organic carbon released during reductive dissolution of goethite mobilizes contaminants by forming metal-organic complexes and by forming iron-containing organic colloids that bind and mobilize contaminants				
4.2.a Reductive dissolution of goethite in Riverton and Slate River TRZs releases DOC and leads to formation of Fe-organic colloids	• Field sampling • Batch experiments	In progress	12-13	• This report
4.2.b Reductively released DOC and/or Fe-organic colloids bind and mobilize U(IV) and U(IV) in Riverton TRZs	• Field sampling • Batch experiments	In progress		• This report
4.2.c Reductively released DOC and/or Fe-organic colloids bind and mobilize Pb(II) in Slate River TRZs	• Field sampling • Sediment characteriz.	In progress	13-14	• This report • PI meeting posters

4.2.d Reductively released DOC and/or Fe-organic colloids bind and mobilize Zn(II) in Slate River TRZs	• Field sampling • Sediment characteriz.	In progress	13-14	• This report • PI meeting posters
4.2.e Reductively released DOC and/or Fe-organic colloids bind and mobilize Mo in Riverton TRZs	Starting FY21	NA	NA	NA
Modeling Task 4.3 Reaction network modeling: impact of TRZ Fe/S redox cycles on contaminant release (coincident w/ Modeling Task 2.2)	Starting FY20	NA	NA	NA

4.a. Review of scientific progress toward achieving program objectives

Subtask 1. Influence of rhizosphere processes on carbon dynamics and contaminant hosting solid phases. *K. Boye (lead)* This subtask is scheduled to begin in FY2019. At the moment of writing, preliminary field data has been collected and rhizoboxes are under construction. Pilot greenhouse experiments are scheduled to begin in Oct 2018.

Subtask 2. Biogeochemical redox responses to hydrological transitions. *K. Maher, C. Francis (co-leads).* In floodplain aquifer systems, contaminant biogeochemistry and transport is strongly influenced by groundwater elevations, flow rates, and direction. At the Riverton site where seasonal redox transitions have been observed, we hypothesized that *TRZ sediments will exhibit large-scale shifts in dominant functional guilds corresponding to oxic (unsaturated) vs. reducing (saturated) conditions (Hyp. 2.3).* The shifts in microbial activity will be reflected most clearly in the chemical composition of porewater and sediments. Thus as a first step towards testing this hypothesis, we conducted a twice-monthly sampling campaign from April through November 2017 to elucidate how hydrologic dynamics impacted soil, pore- and groundwater chemistry and redox condition.

Porewater response to hydrological transitions (modeling tasks 2.1 and 2.2) *C. Bobb (lead), K. Boye, S. Fendorf, J. R. Bargar, K. Maher.* We observed that the Riverton runoff cycle is defined by three dramatically differing flow regimes that drive microbial activity: Stage 1-rising water table (little to no hydraulic gradient, aerobic metabolisms dominate), Stage 2- peak runoff/flood (zero hydraulic gradient, anaerobic metabolisms take over) Stage 3- falling water table (low hydraulic gradient, microbial metabolisms vary based on soil moisture). As runoff from spring snowmelt saturates the aquifer, a reducing front was
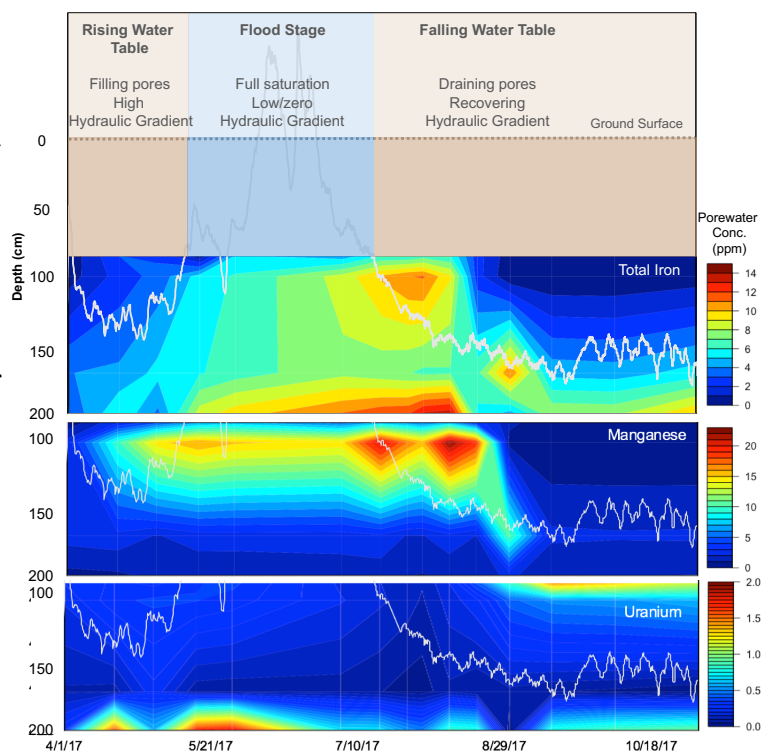
Figure 2. Porewater concentrations of Fe, Mn, and U (top to bottom) in pit 2 in 2017 as a function of depth (y-axis, feet above sea level), represented as heat maps (units of mg/L). Water table depth is indicated by the white line.

observed to propagate upward through the soil profile. Increases in soluble Fe and Mn (**Figure 2**) indicated that reducing conditions reached a maximum within 6 weeks of saturation and were maintained for another 12 weeks.

Significantly, full re-oxidation was not achieved until ten weeks after the water table returned to base flow. This suggests that reduced species (*e.g.*, iron sulfides) buffered redox potential as soils drained and were exposed to air. Maintenance of reduced conditions is a primary control on the mobility of redox sensitive contaminants at this site. Early transients in porewater U at depth indicate oxidative release during periods of high flow rates. The subsequent increase in porewater U, particularly above the water table, suggests reoxidation and supersaturation.

Impact: Accumulation of reduced species (*e.g.,* FeS minerals) buffers U from re-oxygenation, and limits the amount of U re-mobilized via oxidative dissolution. Hence, the duration and spatial extent of reducing conditions, driven by moisture status of the soil, are key controls on U mobility in transiently reduced sediments.

Seasonal changes in sediment redox status and soluble pools of C and U at the Riverton site (supporting modeling tasks 2.1 and 2.2) *K. Boye (lead), C. Bobb, S. Fendorf, J. Bargar.*

We examined the solid phase total and water soluble concentrations of C, nutrients, and contaminants in sediment cores throughout the season. The June 2017 flood (**Fig. 2**) distributed water soluble C relatively evenly throughout the profile (**Fig. 3**). This pool was then quickly depleted below the root zone (*i.e.*, <30 cm), and extending down to the clay layer at 70-90 cm depth. This clay forms a distinct moisture boundary, with sediments above drying relatively quickly and sediments at and below this depth remaining close to saturation throughout the sampling season (data not shown). Microbial respiration measurements indicated that the flood- driven filling of pore space with water caused the microbial community to switch to anaerobic respiration for several weeks, lasting into September at some depths (data not shown). This was consistent with an increase in HCl-extractable Fe(II) after the flood, suggesting a reducing front propagated downwards with time and that the presence of roots prevented the re-oxidation of Fe(II) in the top part of the soil profile (**Fig. 3**).

Impact: Sediment biogeochemistry in shallow sediments at the Riverton site responded strongly to seasonal hydrological triggers (saturation, draining). For example, redox inversion, from oxic to reducing, occurred over much of the shallow sediment profile by mid-summer. However, the specific biogeochemical responses varied with
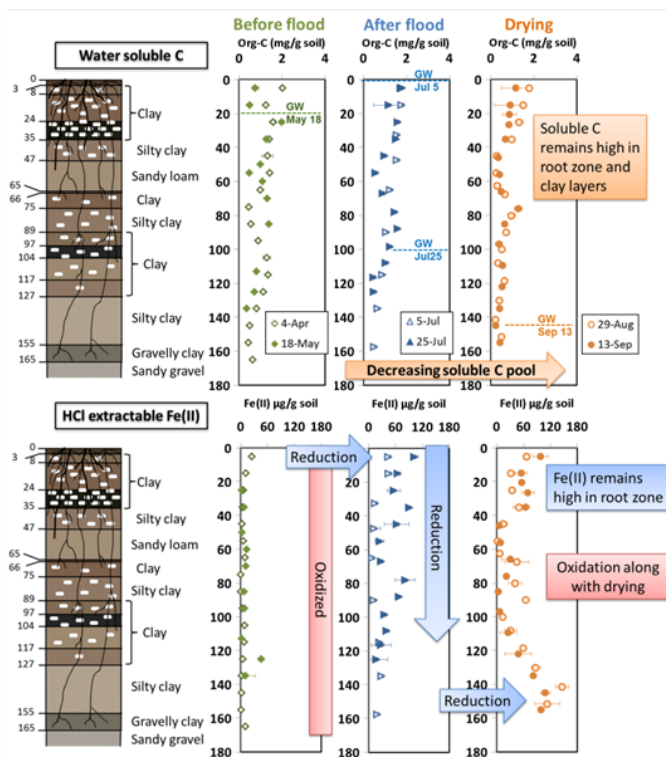
Figure 3. Depth profiles of water extractable C (top) and HCl-extractable Fe(II) (bottom) during the 2017 season at the Riverton, WY, site. Error bars denote 1 standard deviation.

depth and sediment characteristics, indicating that fine-scale physical heterogeneity (often ignored in models) is important and will present modeling challenges. These data provide a conceptual framework for interpreting porewater and groundwater data, planning targeted sampling efforts, and designing laboratory experiments and model representations relevant to field conditions.

Patterns of niche partitioning and diversity reflect environment (Hyp 2.3a) *E. Cardarelli (lead), K. Boye, J. Bargar, C. Francis* Rapid transitions between oxidizing and reducing
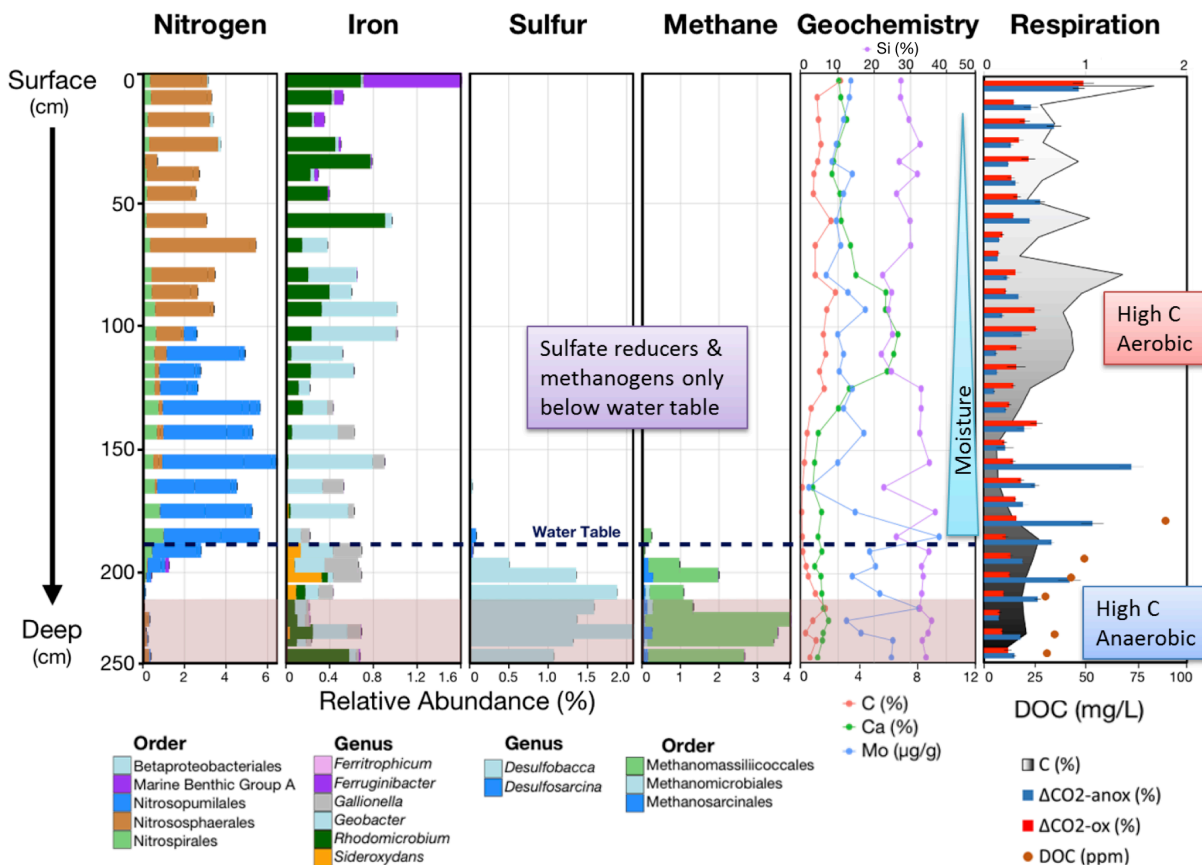

Figure 4. 16S rRNA gene sequence depth profiles of KB1 core (Fig. 1), showing the relative abundance of genera known to be involved in N, Fe, S, and methane cycling. Total concentrations of C, Ca, Mo, and Si are shown in the geochemistry panel and the respiration panel shows measured aerobic and respiration rates together with total C and DOC in porewater. Note the apparent switch to dominant anaerobic respiration in the capillary fringe and coincidental occurrence of sulfate reducers and methanogens below the water table.

conditions (*cf.*, preceding section) are accompanied by intense microbial activity, biogeochemical transformations of carbon and inorganic constituents, and increased nutrient and contaminant fluxes. Yet, little is known about the depth- and time-dependence of the structure and spatial distribution of microbial communities belowground and across the soil-groundwater interface. To address these questions, we collected 82 soil samples from Riverton, WY, and 80 samples collectively from Naturita, CO, Grand Junction, CO, and Shiprock, NM down to 6 m depth. Depth-resolved molecular characterization of the microbial communities paired with detailed geochemical measurements (**Fig. 4**) indicates niche partitioning in the subsurface is influenced by water table interactions.

Early results show that Riverton microbial community data, including subnetworks with abundant functional guild members, have co-occurrence and connectedness patterns involving newly described taxa. Using the number of connections for each node, operational taxonomic units (OTUs) with higher degree centrality scores indicate they have greater connectedness to other taxa in the community. Of the nitrifier subnetwork, the thaumarchaeal family Nitrosopumilales had the greatest number of connections and highest betweenness centrality score. *Geobacter* was determined to link *Thiobacillus* (a chemolithoautotroph) and a broad range of anaerobic, alkaliphilic sulfur-reducing bacteria. Interestingly, methanogenic Methanomassilicoccales are associated with newly described phyla inferred to be symbionts (e.g. Nanoarchaeota, Berkelbacteria, Microgenomates, and Parcubacteria) as well as with taxa now thought to be major constituents in global C cycling (e.g. Rokubacteria and Bathyarchaeota).

Impact: We establish that functional guilds are distributed in depth-specific patterns, which correspond to transitions in the subsurface from unsaturated to water-saturated zones. We confirm nitrifiers are regionally abundant in the unsaturated oxic zone, and decline in abundance as conditions become water-saturated and anoxic.

Using microbial energetics and mass balances for discerning redox trajectories[2] (Hyp. 2.3) *K. Boye (lead), B. Tolar, C. Bobb, C. Francis, J. Bargar, S. Fendorf.* Rapid transition from dry to wet conditions, such as after flooding, triggers a complex network of microbial metabolic processes with variable environmental impacts (*e.g.* fermentation, methanogenesis, nitrification/ denitrification, metal and/or sulfate reduction). To represent such heterogeneous processes in numerical models is a daunting task and simplifications based on erroneous assumptions or inadequate mechanistic understanding can result in flawed predictions of the outcome.
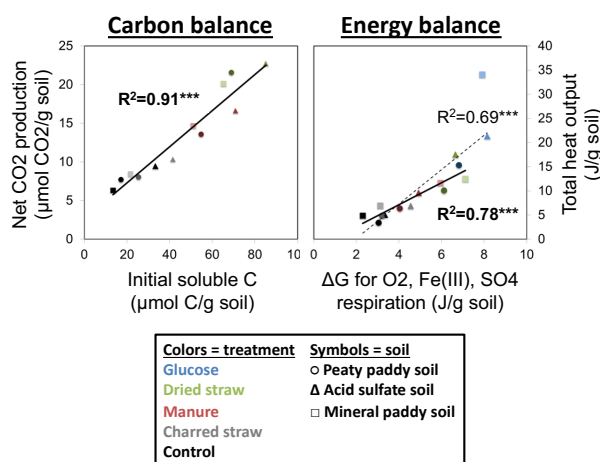
Figure 5. Left: net microbial respiration rates in sediment mesocosms correlate to initial soluble C. Right: Heat output is correlated to ΔG of overall respiration reactions.

In a mesocosm experiment, we studied the effect of soil type and organic substrates on net microbial respiration rates (aerobic respiration and anaerobic iron and sulfate reduction), methanogenesis, and the resulting heat output from metabolic activities during the transition from dry to inundated and subsequent oxygen depleted conditions. We found that the net respiration rate was strongly correlated with the initially available water-soluble organic C pool (**Fig. 5**). Moreover, calculating the energy supplied by C oxidation from this pool with utilized electron acceptors (O_2, $Fe(III)$, SO_4^{2-} were considered) rendered a strong correlation between the Gibbs free energy for the overall respiration reactions and the heat output measured by isothermal microcalorimetry. Evaluations of the calorespirometric ratios (heat output per unit C respired) suggested distinctly different metabolic activities were stimulated by the various organic substrates in the different soils.

Impact: This pioneering study showed that mass and energy balances can provide valuable insights of the metabolic trajectories in complex systems, which have the potential to support more accurate simplifications of microbially mediated redox processes in numerical models.

Subtask 3. Impact of hydrological-biogeochemical coupling on solute transport and groundwater biogeochemistry.
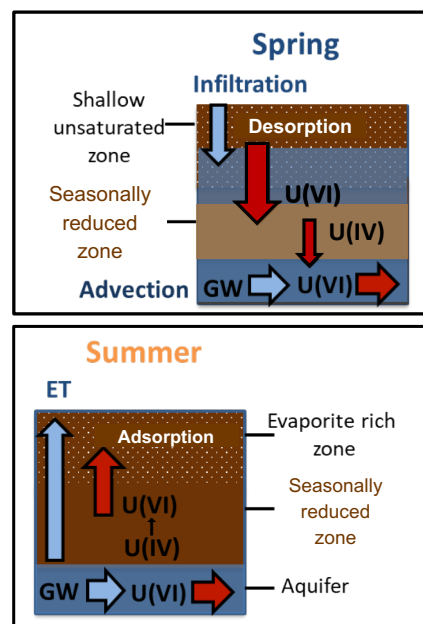
Relevance of vertical transport for U plume sustenance (Hyp. 3.3) *J. Bargar (lead), S. Roycroft, K. Boye, V. Noel., S. Fendorf.* We investigated evaporite-associated U speciation at Riverton between May 2015 – Sept 2016, which included a 3-week long flooding event starting on May 8, 2016. Sediment cores were collected in spring and late summer both years, at two locations: well 855 (TRZ present) and at upgradient well 858 (no TRZ observed). Chemical extractions were completed in FY2018 and provided the following key findings:

- *Downward vertical transport of shallow U (< 80 cm depth) is important.* At site 855, sediment concentration profiles indicated that 5.6 g U /m^2 (or ~20% of total shallow U pool) was flushed downward between Aug 31, 2015 and June 1, 2016, presumably during flood inundation. A large pool of strongly sorbed uranium accounted for the majority of mobilized mass. The much smaller pools of evaporite and cation-exchangeable U were also flushed downward. The reduced zone also lost a large fraction (1.4 g U/m^2) of its U pool, presumably due to drainage of waterlogged soils and discharge into the aquifer.

- *U is rapidly transported **upwards** during the summer.* Between June 1 and Aug 15, 2016, 2.2 g U /m^2 moved from the TRZ back up into shallow sediments. Upward mobilization is attributed to strong evapotranspiration.

- *Multiple geochemical processes operate simultaneously.* Sorption/ desorption, evaporite precipitation/ dissolution, and cation exchange occur simultaneously and compete for U. Silicate was the dominant host for U and most likely precipitating alongside sulfate and carbonate evaporites. U accumulation in the TRZ strongly implies that reduction of mobile U(VI) to less mobile U(IV) is also important.

- *Redox-active zones enhance upward transport and accumulation of U.* At site 855, 20% of flushed U was retained within the underlying reduced zone. Subsequently a large fraction of this U was mobilized back up to shallow sediments. Thus, transient redox-active zones strongly enhance accumulation of U and prolong plume persistence.

Impact: This example demonstrates dramatically the impact of hydrological triggers on U biogeochemistry and mobilization. The coupling between lateral and horizontal migration controls the overall rate of U transport across the floodplain (**Fig. 6**).

Figure 6. Conceptual model of U transport at Riverton. **Spring** flooding flushes U downward, simultaneously triggering reducing conditions. U(VI) entering the TRZ is reduced and accumulates as U(IV). **Summer** draining leads to oxidation of U(IV) back to U(VI), which is mobilized upward by strong capillary rise.

Subtask 4. Mechanisms controlling release/uptake of nutrients and contaminants.

Hydrological perturbations and redox cycling: generators of colloids? (Hyp. 4.2.a) *V. Noël, K. Boye, J.R. Bargar; N. Kumar (Stanford); R. Cory (Michigan).* Sediment-water interactions driven by wet-dry cycling medaite mineral transformations and organic C degradation and alter the mobility of sediment constituents. The reactivity of mineral and organic phases in response to wet-dry cycling can generate colloids that can bind to anions, trace metals, and radioisotopes,

thereby enhancing their mobility. Knowledge of the nature of mobilized phases is sparse but needed to predict contaminant mobility and short- and long-term impacts on water quality.

We have previously found that iron oxides and organic matter exhibit strong reactivity tied to wet-dry and redox cycling[2,4,6]. We have subsequently followed organo-mineral phase responses to (1) re-wetting and (2) reducing conditions to characterize mobilized phases.
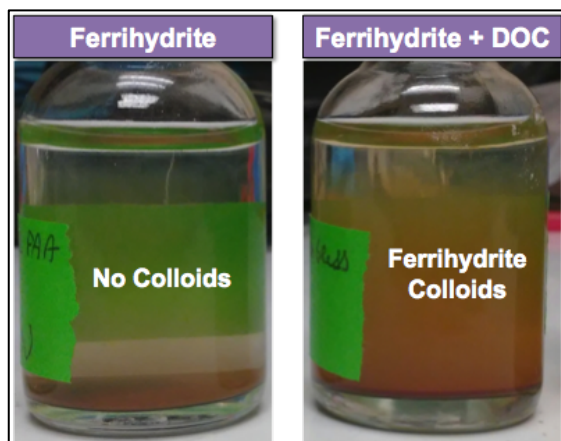
1. Mobilization of iron oxide nanoparticles in newly-saturated sediment. Re-wetting of organic-enriched sediments is expected to release dissolved organic carbon (DOC). Preliminary results show clearly that DOC released from newly-saturated conditions can trap iron oxide nanoparticles and enhance their mobility (**Fig. 7**).

2. Reductive dissolution of iron oxides promotes colloid formation. Once sediments are water saturated, reducing conditions establish and, in UCRB sediments, promote sulfidation[6], as well as the dissolution of reduction-sensitive iron oxides. We investigated the nature of mobilized phases from the reductive dissolution of iron oxides in presence of sulfides[3]. Our results systematically revealed the generation of polysulfides and elemental sulfur. Interestingly, we observed that the concentration of sulfides relative to iron oxides (S/Fe ratio) controls the sulfidation mechanism and subsequently the nature of products generated (**Fig. 8**):

- Low sulfide concentration (S/Fe ratio ≤0.5): iron dissolution => release of dissolved Fe(II)
- High sulfide concentration (S/Fe ratio >0.5): formation of FeS nanoparticles.

Impact: The S/Fe ratio and DOC concentration are key regulators of the extent and nature of colloid formation. At low sulfide concentrations, Fe(II) is released and expected to be sorbed by DOC (Noël et al., 2018 in prep), whereas at high sulfide concentrations FeS nanoparticles are expected to complex with DOC, thus, inhibiting their aggregation and enhancing their transport.

Confirmation of redox transitions in Slate River floodplains of relevance for Pb and Zn mobility (Hyp. 4.2.c, 4.2.d) *J. Bargar (lead), C. Dewey.* Slate River in Gunnison County, CO, is adjacent to the LBNL Watershed Function SFA study area, but unlike East River, Slate River is impacted by upstream hard rock mining. In Aug and Oct 2017, we conducted initial sampling of Slate River floodplains to estimate Pb and Zn contaminant inventories and to test the hypotheses that: (i) well-developed vertical redox transitions are present, and (ii) water table variability causes the oxic-anoxic transition to rise and fall in response to changing soil moisture. These hypotheses are implicit to hypotheses 4.1 and 4.2; verifying their validity was a necessary prerequisite to expanding the

Figure 7. In absence of soluble organic carbon (On the left): settling ferrihydrite nanoparticles. In presence of soluble organic carbon (On the right): mobilization of ferrihydrite nanoparticles..
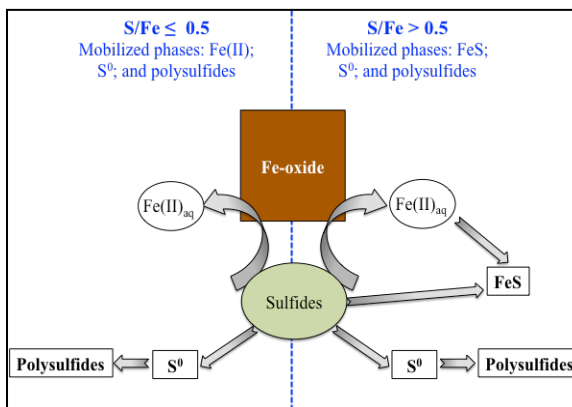
Figure 8. Schematic representation of the reaction pathways of sulfidation of Fe(III)-oxides and nature of generated colloids/nanoparticles.

Slate River research program.

- *Contaminant burdens*. Samples from a shallow floodplain along the west side of Slate River contains an estimated 54,000 kg of Zn and 30,000 kg of Pb, two of the most abundant contaminants of concern in these drainages.

- *Redox transitions are present and respond rapidly to soil moisture changes.* Redoximorphic features with gley colors were present at/above the water table (**Fig. 9**), confirming hypothesis (i). Subsequently, sulfur K-edge XANES analyses showed that pyrite (FeS_2) was the dominant form of reduced S, with high abundance below the water table. Oxidized S was present as organo-sulfate and inorganic sulfate, most abundantly above the water table. Between Aug 27 and Oct 6, four distinct rainfall events caused the water table to rise by *ca* 30 cm to a depth of 60 cm. The 80-90 cm interval became saturated during this change, and simultaneously, the ratio of pyrite to sulfate increased. This behavior indicates that reducing conditions rapidly onset following inundation, confirming hypothesis (ii).

The low ratio of mackinawite (FeS) to pyrite, a metastable intermediate in the formation of pyrite, can be caused by influxes of oxygen[6]. It is plausible that dissolved oxygen in river water was transported into the reduced zones from the underlying highly conductive cobble layer. Measurements in summer/fall 2018 will examine this question, as well as the behavior of Pb(II) and Zn(II) in response to hydrological changes.

Figure 9. Slate R. sediments (numbers indicate depth in cm) showing orange and gley redoximorphic coloration.

Impact: The presence of redox transiency at Slate River floodplains has implications for Pb(II) and Zn(II) behavior. Both co-precipitate in sulfides and associate strongly with iron oxides. During redox transitions, dissolution of these solids will cause Pb(II) and Zn(II) to be released and mobilized. Under these conditions, abundant organo-S groups may be important for binding Pb(II).

Impact of organic matter type on U complexation in anoxic sediments (Hyp. 4.2b, in 2014 Science Plan) *S.E. Bone (lead), J. Cliff (EMSL), S. Roycroft, M. R. Cahill, S. Fendorf, J.R. Bargar.* To understand U(IV) behavior in the anoxic sediments where it accumulates, it is essential to understand its chemical form. Bone et al.[4] provided direct evidence that U(IV) was physically associated with organic matter in a model system analogous to high-organic matter sediments; however, a more complete description of the organic binding environments in which U(IV) exists in real sediments is needed. We therefore examined the association of U(IV) with organic matter in sediments collected from the legacy ore-processing site near Riverton, WY.

Density fractionation is a relatively gentle method for separating organic and mineral components of soils, without altering organo-mineral associations or the chemical composition of organic matter. Such separation enables us to more easily assess the relative importance of these two classes of sorbents for U. To this end, we performed density fractionation on two reducing sediments containing > 100 ppm U (50 – 90 % as U(IV)). We recovered the following fractions: (1) a particulate organic carbon (POC), or "mineral-free" fraction, (2) an organo-mineral fraction and (3) a "mineral" fraction[32-34]. Each of these fractions was examined using a combination of scanning transmission X-ray microscopy (STXM; organic and mineral distribution and organic speciation) and nano-secondary ion mass spectrometry (NanoSIMS; elemental distribution).
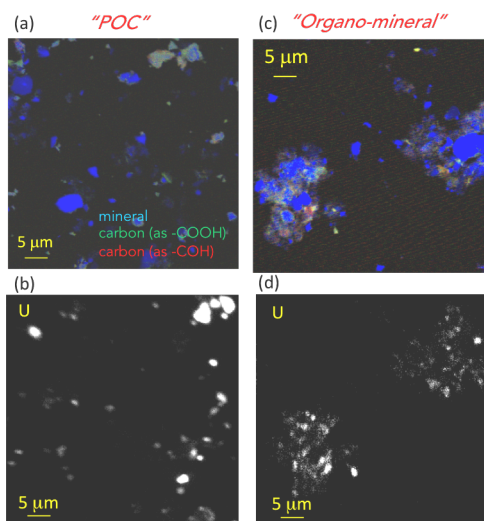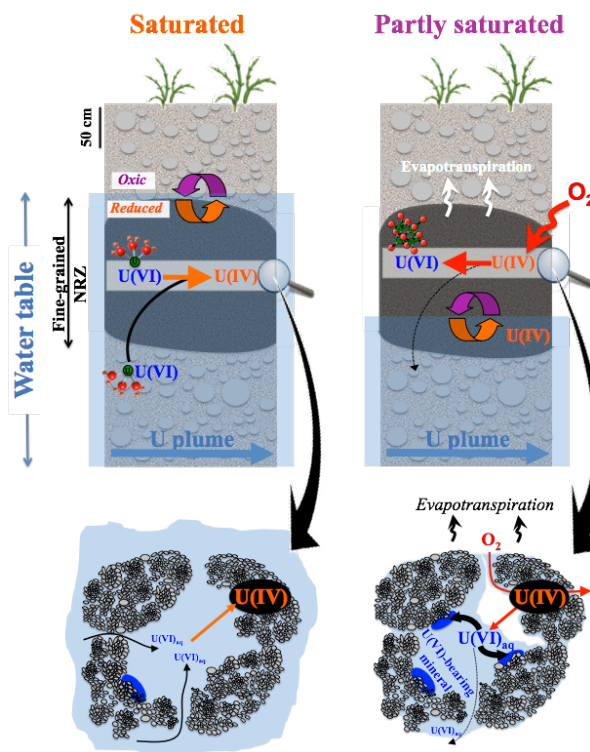
Figure 10. Distribution of minerals, organic carbon and U in POC and organo-mineral sediment fractions. (a) STXM image of minerals (blue) and organics (green=carboxylates and red=alcohol functional groups) in POC. (b) NanoSIMS-derived distribution of U for particles shown in (a). (c) STXM image of minerals and organics in organo-mineral fraction. (d) NanoSIMS-derived distribution of U for particles shown in (c).

The organic matter content was found to be a strong determinant of the U content within each fraction. At the nano-scale, in both sediment samples, U was associated with diverse types of organic matter, including plant material (such as lignin), partially-degraded organic matter, and microbial material. Our results further reveal that sedimentary U that is physically associated with organic materials is typically also physically associated with inorganic phases (**Fig. 10**).

Impact: Organic matter is the primary sorbent for U (largely as U(IV)) in contaminated sediments, although much of the organic matter with which U is associated is also associated with minerals. Many types of organic materials were physically associated with U, including those originating from phenol-rich lignin, not just microbial material which has been shown to be a highly effective U(IV) sorbent. This knowledge can be used to derive new models for U(IV) complexation under field-relevant conditions.

U-storage mechanism driven by wet-dry redox cycling (Hyp. 4.2, in 2014 Science Plan) *V. Noël, K. Boye, J.R. Bargar; R.K. Kukkadapu (EMSL)*. Aquifers in the Upper CRB exhibit persistent U groundwater plumes originating from former ore processing operations. Our previous field studies suggest that sulfidic, organic-enriched sediments, referred to as 'naturally reduced zones' (NRZs), are regionally common throughout the upper CRB[6] and that they strongly accumulate U[7]. In fine-grained NRZs, where low permeability and permanent water saturation promotes stable anoxia, we have observed that "non-crystalline" U(IV) dominates[7]. However, NRZs can also exist within the zone of water table fluctuations, where they will be subject to seasonal or episodic drying and intrusion of oxygen. U retained in its reduced form is sensitive to oxidation, which may induce re-release of U to the aquifer. Crucially, no studies have documented the impact of episodic wet-dry

Figure 11. Conceptual model for the 'oxidative stabilization' of U in fine-textured NRZs in fluctuating water saturation conditions[2]. STEP 1: water saturation induces anoxia that promotes accumulation of non-crystalline U(IV). STEP 2: partly saturated conditions allow oxidants to diffuse and oxidize U(IV) to U(VI) that accumulates in the porewater due to limited transport out of fine-textured NRZs.

cycles on U(IV) behavior in low-permeability NRZs in the field.

In a study of NRZs within the zone of water table fluctuations at the Shiprock, NM, site, we:

- Confirmed that reducing conditions are needed to accumulate U
- Showed redox cycling can promote U(VI) accumulation in equal proportion to U(IV), contradicting widely held expectation that U(VI) is always mobilized (can't accumulate).
- Propose a new conceptual model, where redox oscillations driven by annual water table fluctuations and strong ET promote conversion of U(IV) to relatively immobile U(VI) in low permeability sediments (**Fig. 11**)

Impact: These results suggest long-term U stabilization promoted by redox oscillations. This observation contradicts the common idea that U(IV) accumulated in reducing conditions is systematically mobilized to groundwater during re-oxidation.

Kinetic inhibition of U reduction in calcium carbonato uranyl complexes (Hyp. 2.2 in 2014 Science Plan) *C. Dewey (lead), J. Bargar, S. Fendorf*. Reduction of the calcium carbonato uranyl species is inhibited, but whether this inhibition arises from a thermodynamic restriction or a kinetic constraint is unresolved. Using Fe(II)(aq) as a model reductant, we revealed that reduction of the calcium carbonato uranyl species is kinetically inhibited. We measured the extent of U(VI) reduction in solutions with different concentrations of calcium and carbonate, and thus different proportions of the calcium carbonato uranyl species, over 100 h (**Fig. 12**). In all reactors, as U(VI) was reduced and removed from solution, U speciation approached 100% calcium carbonato uranyl. Concurrent with this change in speciation, the rate of U(VI) reduction approached zero, despite thermodynamic conditions being theoretically favorable for reduction. A pseudo first-order kinetic model described reduction of the dominant non-calcium species across reactors, suggesting that reduction of these species was the dominant reduction pathway. Further, in all reactors, the total reduced U was directly related to the initial proportion of non-calcium uranyl species. In addition, we found that the uranium reduction product in our system was a mixed U(V)/U(VI) phase, likely with trace amounts of incorporated Fe.
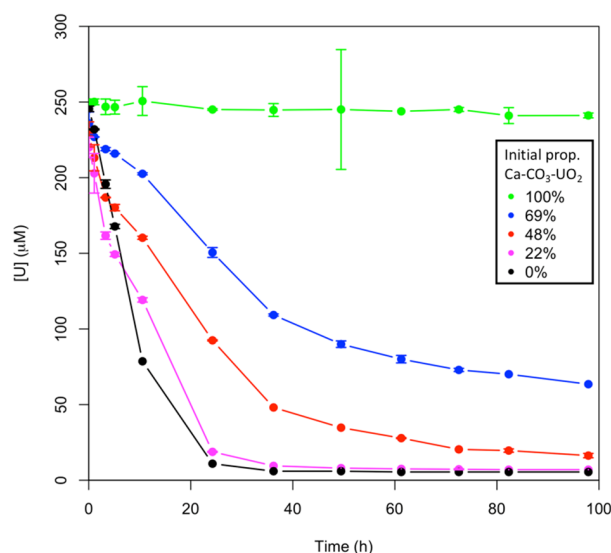
Figure 12. Aqueous concentrations of U(VI) over reaction time. Removal of U(VI) from solution occurs via reduction. The extent of U reduction is directly related to the proportion of non-calcium U(VI) species. With increased initial proportion of calcium carbonato uranyl species, the extent of U reduction decreased and uranyl species approached 100% calcium carbonato uranyl (not shown). Concurrently, the rate of U reduction approaches a limit (apparent after ~40 h).

Impact: This finding points to a novel U(VI) reduction pathway, and it lays the foundation for further research on the conditions that favor U(V) over U(IV) reduction products.

4.b. Future scientific goals, vision, and plans toward meeting program objectives

One year into the program, the Groundwater Quality SFA Science Plan remains current and well aligned with the Biogeochemistry Grand Challenges set forth in the new CESD Strategic Plan, especially challenges 3, 5, and 6. Research progress to date suggests that the work plan will make substantial and exciting contributions toward CESD strategic goals. Consequently, we believe it is strategically valuable to continue the execution of our existing Science Plan.

Over the next 12 months, we will focus on collecting high-quality seasonal (spring-summer-fall) field samples at both the Riverton, WY and Slate River, CO sites. We will complete a biogeochemical reactive transport model that simulates redox thresholds at Riverton (Modeling subtask 2.2) and shift to building a more complete, and accurate model representation of Fe and S redox cycling believed to be critical to water quality behavior (Modeling subtask 2.2). We will also initiate modeling of the advective coupling of TRZs and the unsaturated zone (Modeling subtask 3.4). We will wrap up experimental subtasks 2.3.a (abundance patterns of nitrifiers during redox cycling), 3.1 (contaminant sequestration and nutrient release from reduced zones), and three geochemistry activities that test for colloid generation during onset of reducing conditions, particularly sulfide colloids (Subtask 4.1.2), and DOC and organic-Fe colloids (Subtask 4.2.a) and examine their impact on U mobilization (Subtask 4.2.b). As these activities complete, we plan to initiate experimental activity in Subtasks 1.1 (impact of roots on mineral precipitates), and 2.3.b (impact of Mo abundance on nitrate-reducing communities). We will also focus on completing and submitting manuscripts in progress.

4.c. New scientific results that may shift current research focus areas and/or identified knowledge gaps in the program

We will begin investigating the potential value of two ideas, each of which could modify our research focus in the out years. (i) We have developed a collaboration with Rose Cory (U. Michigan) to investigate the impact of iron-generated reactive oxygen species on organic matter degradation. The Cory group has shown that abiotic Fe-catalyzed oxidation of NOM can account for half or more of NOM mineralization/CO_2 production in thawing Arctic tundra soil pore water[35] The conditions necessary for these reactions to progress (presence of DOM, soluble Fe(II), and low concentrations of O_2) are expected to be present in TRZs at the onset of the drying/oxidation phase. Consequently, these reactions may have an important impact on consumption of NOM, the quality and abundance of DOM, and metals behavior. As resources allow, we plan to strategically investigate the importance of these reactions. (ii) We see an opportunity to team up with ESS-DIVE, SSRL, and EMSL to help create community resources based on existing and new synchrotron data collected by BER-CESD-funded researchers. While such an effort would likely entail a multi-year collaborative effort, it could have a large and catalytic impact on CESD scientific discoveries. Therefore, as resources allow, we intend to investigate how to create a new project in this area in collaboration with ESS-DIVE.

4.d. Collaborative research activities with external researchers

The Groundwater Quality SFA has significant collaborations with the following groups:

Science Scientific User Facilities:

- EMSL: Malak Tfaily: carbon characterization (FT-ICR-MS), John Cliff - NanoSIMS isotope imaging, and Ravi Kukkadapu - Mössbauer spectroscopy. (Subtasks 1, 2 and 4)
- JGI: Trent Northen: metabolomics. (ST 2)

- CLS: Jay Dynes: STXM of colloids and organo-metal complexes. (ST 4)

DOE National laboratories:
- LBNL: Ken Williams: Pb and Zn behavior in the Slate River watershed (ST 4)

Non-Science DOE Offices:
- DOE-LM: Ray Johnson (Navarro): U groundwater dynamics at the Riverton site (ST 2)

Academic collaborators:
- Rose Cory (U. Michigan): Reactivity of Fe-organic matter colloids (ST 4)
- S. Fendorf (Stanford): Iron-carbon interactions and metal redox transformations (ST 4)
- Jon-Petter Gustafsson, Dan Berggren (SLU, Sweden): Colloid transport in soils (ST 4)
- Anke Herrmann (SLU, Sweden): Microbial energetics, micro-calorimetry (ST 2)
- L. Meredith (U. Arizona): Microbe-mediated trace gas flux analysis (ST 4)
- K. Maher (Stanford): Carbon reactive transport modeling (ST 2)
- G. Morin (Sorbonne Université): Inorganic geochemistry of Zn (ST 4)
- Anders Tunlid, Per Persson (Lund University) – Reactivity of Fe-organic complexes (ST 4)
- Karrie Weber (U. Nebraska): Impact of N cycling on U redox and mobility in TRZs (ST 4)

5. Staffing and budget summary

5.a. Funding allocation by program element (task) and individual researcher

In FY2018, subtasks 2, 3, and 4 comprise about 45%, 30%, and 25% of the total effort, respectively. The largest cost is salaries for postdoctorals and early career scientists. Support for senior personnel is a small fraction of the total salary expenditure. Roles and effort for each researcher are reported in Table 2.

Leveraging. DOE funds are leveraged through collaborations with independently-funded postdoctoral and Stanford graduate students, including: C. Bobb (biogeochemical reactive transport modeling), E. Cardarelli (microbial N cycling), N. Kumar (Fe/S redox cycling), C. Dewey (U complexation, Slate River field work), and Z. Perzan (geophysical measurements and transport modeling). The Water Quality SFA provides supplies and field logistics to support research projects conducted by these individuals, which encompass portions of the Science Plan.

DOE-LM supports access to the Riverton field site and has provided funding to help support research performed by S. Roycroft and Z. Perzan.

Scientific user facilities. We are conducting work at EMSL, JGI, and SSRL. We recently submitted a proposal to the FY2018 FICUS call to support our microbial 'omics', mineral transformation, and colloid transport research.

5.b. Funding allocation to external collaborators

A subcontract provides salary support to S. Benner (Boise State University) to perform field hydrology measurements at the Riverton site (**Table 2**). A subcontract to Dr. Jackie Klancher (Central Wyoming College, CWC) provides support for sampling activities at the Riverton site.

5.c. Personnel actions and procedures

B. Tolar was recruited to join the SLAC SFA team. At present we are recruiting a postdoc to lead our unsaturated zone reactive transport modeling activity.

Table 2. Specific roles of research personnel in FY 2018

Personnel	Title	Expertise	Role	Subtask	Effort (months)
John Bargar (SLAC/SSRL)	Senior scientist	Biogeochemistry, X-ray spectroscopy	Lead PI, Research manager, Scientific lead for subtask 4, Field experiment (Zn) lead, Slate R.	4	3.6
Shawn Benner (Boise State)	Associate professor	Hydrology	Field hydrology experiments	2, 3	1
Callum Bobb (Stanford)	Student	Biogeochemistry	Field experiments, Reactive transport modeling	2	Travel, supplies*
Kristin Boye (SLAC/SSRL)	Staff Scientist	Biogeochemistry, soils science	Scientific lead for subtask 1, Field experiment lead, Riverton, laboratory experiments	1, 3	12
Emily Cardarelli (Stanford)	Student	Molecular microbiology	Field and laboratory experiments, gene sequencing	2, 4	Travel, supplies*
Christian Dewey (Stanford)	Student	Biogeochemistry	Field experiments (Pb), Slate R.	4	Travel, supplies*
Scott Fendorf (Stanford)	Professor	Biogeochemistry, soils science	Scientific lead for subtask 3	3	0.5
Jacki Klancher (CWC)	Associate professor	Water quality assessment	Lead for Riverton field intern team	1-4	Field sampling
Naresh Kumar (Stanford)	Postdoc	Geochemistry	Laboratory experiments	3	Travel, supplies*
Chris Francis (Stanford)	Professor	Molecular microbial ecology	Scientific co-lead	2, 3, 4	0.5
Katharine Maher (Stanford)	Associate professor	Geochemical modeling, reactive transport	Scientific lead for subtask 2	2	0.5
Vincent Noël (SLAC/SSRL)	Postdoc	Biogeochemistry	Field and laboratory experiments	4	12
Zachary Perzan (Stanford)	Student	Geochemistry	Field experiments and hydrological modeling	3	Travel, supplies*
Scott Roycroft (Stanford)	Student	Soils science	Field and laboratory experiments	4	Travel, supplies*
Bradley Tolar (SLAC/SSRL)	Postdoc	Molecular microbiology	Field and laboratory experiments, gene sequencing	2, 4	12

* Salary support for this student is provided by fellowship funding or non-SFA funds (leveraging).

5.d. National Laboratory investment in the program

SSRL provides salary and admin support for Bargar that covers part of the SFA management effort. SSRL operates the SPEAR3 synchrotron facility and x-ray beam lines that we use.

5.e. Capital Equipment needs (future)

Two major instrumentationcapabilities are identified that would strategically enhance the scientific impact of the Groundwater Quality SFA program and the leadership of the SBR program in the international scientific community. While not capital equipment, these items are expensive and difficult to accommodate in our current budget.

1. Complete set of in-situ sensors for O_2, CO_2, H_2 and redox species for deployment at the Riverton site to support our modeling efforts (modeling tasks 2.1 and 2.2), as well as increasing our understanding of the redox dynamics at field scale. Currently, we are dependent on weekly manual sampling of porewater to document redox status, which is insufficient to document rapid changes in redox conditions. Moreover, it is very difficult to measure DO in the unsaturated zone using poreware. Yet, this information is needed to develop a robust understanding of redox transitions in response to hydrological perturbations, which is the foundation for our Science Plan. Sensors are well suited for such measurements because they can be embedded directly in the sediment matrix and directly measure analyte concentrations in pore water.

The cost for a complete set of sensors is estimated to be $50,000.

2. An isothermal nano-calorimetry system for monitoring heat flow from biogeochemical reactions. We recently showed that isothermal *micro*-calorimetry combined with respiration measurements can help decipher microbial metabolic processes in soils[2]. This method has the potential to strongly enhance our science program by constraining the kinetics and thermodynamics related to redox inversions (subtask 2), contaminant reactions (subtask 4), and root-mediated reaction dynamics (subtask 1). No such instrument exists within the SBR SFA portfolio, so we have used the micro-calorimeter in Anke Herrmann's group (Swedish University of Agricultural Sciences). However, access to this instrument is limited, and we have found that we need higher resolution than it is capable of providing.

Isothermal *nano*-calorimetry provides higher temperature sensitivity and can detect heat production from lower-energy yielding metabolic processes, such as fermentation and anaerobic respiration, while facilitating simultaneous measurement of CO_2, O_2, and other chemical species. In spite of its enormous potential[36-38], nano-calorimetry is not being used for biogeochemical research at any of the U.S. national user facilities or laboratories.

We would like to purchase a nano-calorimeter to strengthen our science program and provide a new resource for all of the SBR SFAs to use. SLAC SFA microbial energetics and calorimetry measurements are led by Kristin Boye, a rising early career scientisit, and if funded this project would grow into an integral part of the SFA program.

The cost for a complete TAM IV instrument configured for nano-calorimetry measurements and simultaneous CO_2, O_2, and electrode measurements, including start-up kits of consumables is estimated to be $300,000. If necessary, this system could be purchased in two phases.

References Cited. Citations 1-21 are listed in Appendix A.

31. Climate and Environmental Science Division Strategic Plan 2018-2023; **32**. Kaiser, K. & Guggenberger, G. Distribution of hydrous aluminum and iron over density fractions depends on organic matter load and ultrasonic dispersion. Geoderma 140, 140-146 (2007); **33**. Chenu, C. & Plante, A. F. Clay-sized organo-mineral complexes in a cultivation chronosequence: revisiting the concept of the 'primary organo-mineral complex'. Europ J Soil Sci 57, 596-607 (2006); **34**. Moni, C. et al. Density fractions versus size separates: does physical fractionation isolate functional soil compartments? Biogeosciences 9, 5181-5197 (2012); **35.** Trusiak, A. et al. The role of iron and reactive oxygen species in the production of CO_2 in arctic soil waters. Geochim Cosmochim Acta (2018); **36**. Barros, N. et al. Factors influencing the calorespirometric ratios of soil microbial metabolism. Soil Biol Biochem 92, 221-229 (2016); **37**. Bölscher, T. et al. Differences in substrate use efficiency: impacts of microbial community composition, land use management, and substrate complexity. Biol. fertil. soils 52, 547-559 (2016); **38**. Herrmann, A. M. & Bölscher, T. Simultaneous screening of microbial energetics and CO2 respiration in soil samples from different ecosystems. Soil Biol. Biochem.83, 88-92 (2015).

Appendix A. List of publications and presentations

6.a. Comprehensive list of publications (Published, in press, and submitted) wholly or partly supported by this program, Feb 1, 2017 – June 30, 2018.

1. Noël, V., Boye, K., Kukkadapu, R. K., Lezama Pacheco, J. S., Bone, S. E., Cardarelli, E., and Bargar J. R. (in review) U-storage mechanism driven by wet-dry redox cycling in fine-grained sediments. *Water Research*

2. Boye, K., Herrmann, A. M., Schaefer, M. V., Tfaily, M. M. and Fendorf, S. (2018). Discerning Microbially Mediated Processes During Redox Transids tions in Flooded Soils Using Carbon and Energy Balances. *Front Environ Sci* 6: 15. doi: 10.3389/fenvs.2018.00015

3. Kumar, N., Lezama Pacheco, J. S., Noël, V., Dubket, G., and Brown, G. E. (2018) Sulfidation Mechanisms of Fe(III)-(oxyhydr)oxide Nanoparticles: A Spectroscopic Study. *Environmental Science: Nano* 5(4): 1012-1026. doi: 10.1039/C7EN01109A

4. Bone, S. E., Dynes, J. J., Cliff, J. and Bargar, J. R. (2017) Uranium(IV) adsorption by natural organic matter in sediments. *Proceedings of the National Academy of Sciences of the United States of America* 114(4): 711-716. doi: 10.1073/pnas.1611918114

5. Boye, K., Noël, V., Tfaily, M. M., Bone, S. E., Williams, K. H., Bargar, J. R. and Fendorf, S. (2017) Thermodynamically controlled preservation of organic carbon in floodplains. *Nature Geoscience* 10: 415-419. doi: 10.1038/ngeo2940

6. Noël, V., Boye, K., Kukkadapu, R. K., Bone, S. E, Lezama Pacheco, J. S., Cardarelli, E. L., Janot, N., Fendorf, S., Williams, K. H. and Bargar, J. R. (2017) Understanding controls on redox processes in floodplain sediments of the Upper Colorado River Basin. *Science of the Total Environment* 603-604: 663-675. 10.1016/j.scitotenv.2017.01.109

7. Noël, V., Boye, K., Lezama Pacheco, J. S., Bone, S. E., Janot, N., Cardarelli, E., Williams, K. H. and Bargar, J. R. (2017). Redox controls over the stability of U(IV) in floodplains of the Upper Colorado River Basin. *Environmental Science & Technology*. 51(19): 10954-10964. doi: 10.1021/acs.est.7b02203

8. Boye, K., Lezama Pacheco, J. S. and Fendorf, S. (2017). Relevance of Reactive Fe:S Ratios for Sulfur Impacts on Arsenic Uptake by Rice. *Soil Systems* 1(1): 1. doi: 10.3390/soils1010001

9. Stubbs, J. E., Biwer, C. A., Chaka, A. M., Ilton, E. S., Bargar, J. R. and Eng, P. J. (2017). Oxidative corrosion of the UO2 (001) surface. *Langmuir* 33(46), 13189-13196. doi: 10.1021/acs.langmuir.7b02800

10. Flores Orozco, A., Gallistl, J., Bücker, M. and Williams, K. H. (2017). Decay curve analysis for data-error quantification in time-domain induced polarization imaging. *Geophysics* 83(2), E75-E86. doi: 10.1190/geo2016-0714.1

Manuscripts from collaborations with external groups

11. Meredith, L. K., Ogée, J., Boye, K., Singer, E., Wingate, L., von Sperber, C., Sengupta, A., Whelan, M., Pang, E., Keiluweit, M., Brüggermann, N., Berry, J. A. and Welander, P. W. (in review). Soil exchange rates of COS and CO18O differ with the diversity of microbial communities and their carbonic anhydrase enzymes. *ISME Journal*.

12. Löv, Å., Cornelis, G., Larsbo, M., Persson, I., Sjöstedt, C., Gustafsson, J. P., Boye, K. and Kleja, D. B. (in review). Particle and colloid facilitated Pb leaching in four historically contaminated soils – Speciation and effect of irrigation intensity. *Applied Geochemistry*.

13. Hsu, H. T., Lawrence, C. R., Winnick, M. J., Bargar, J. R. and Maher, K. (2018). A molecular investigation of soil organic carbon composition across a subalpine catchment. *Soil systems* 2(1): 6. doi: 10.3390/soils2010006

14. Sjöstedt, C., Löv, Å., Olivecrona, Z., Boye, K. and Kleja, D. B. (2018). Improved geochemical modeling of lead solubility in contaminated soils by considering colloidal fractions and solid phase EXAFS speciation. *Applied Geochemistry* 92: 110-120. doi: 10.1016/j.apgeochem.2018.01.014

15. Meredith, L. K., Boye, K., Youngerman, C., Whelan, M., Ogée, J., Sauze, J. and Wingate, L. (2018). Coupled biological and abiotic mechanisms driving carbonyl sulfide production in soils. *Soil Systems* 2(3): 37. doi: 10.3390/soilsystems2030037

16. Yabusaki, S., Wilkins, M. J., Fang, Y., Williams, K. H., Arora, B., Bargar, J. R., Beller, H., Bouskill, N., Brodie, E., Christensen, J., Conrad, M., Danczak, R., King, E., Spycher, N., Steefel, C., Tokunaga, T., Versteeg, R., Waichler, S. and Wainright, H. (2017) Water Table Dynamics and Biogeochemical Cycling in a Shallow, Variably-Saturated Floodplain. *Environmental Science & Technology* 51(6): 3307–3317, doi: 10.1021/acs.est.6b04873

17. Dublet, G., Lezama-Pacheco, J. S., Bargar, J. R., Fendorf, S., Kumar, N., Lowry, G. V. and Brown, G. E. (2017). Partitioning of uranyl between ferrihydrite and humic substances at acidic and circumneutral pH. *Geochimica et Cosmochimica Acta* 215(15): 122-140. 10.1016/j.gca.2017.07.013

18. Hausladen, D. M. and Fendorf, S. (2017) Hexavalent chromium generation within naturally structured soils and sediments. *Environmental Science & Technology* 51: 2058-2067. doi: 10.1021/acs.est.6b04039

Manuscripts based on prior graduate studies and partly supported by this project

19. Juillot F., Noël V., Gelabert A., Jouvin D., Louvat P., Göttlicher J., Belin S., Mueller B., Morin G. and Voegelin A.(in review). Zn isotopes and XAS speciation reveal past eutrophication events in continental sediments (Baldeggersee, Switzerland). *Geochimica Cosmochimica Acta*.

20. Noël, V., Juillot, F., Morin, G., Marchand, C., Ona-Nguema, G., Viollier, E., Prévot, F., Dublet, G., Maillot, F., Delbes, L., Marakovic, G., Bargar, J. R. and Brown, G. E. (2017). Oxidation of Ni-Rich Mangrove Sediments after Isolation from the Sea (Dumbea Bay, New Caledonia): Fe and Ni Behavior and Environmental Implications. *ACS Earth and Space Chemistry*. 1(8): 455-464. doi: 10.1021/acsearthspacechem.7b00005

21. Nicolás, C., Almeida, J.P., Ellström, M., Bahr, A., Bone, S. E., Rosenstock, N.P., Bargar, J. R., Tunlid, A., Persson, P. and Wallander, H. (2017). Chemical changes in organic matter after fungal colonization in a nitrogen fertilized and unfertilized Norway spruce forest. *Plant and Soil* 419(1-2): 113-126. doi: 10.1007/s11104-017-3324-8

6.b. Presentations at National and International Scientific Meetings wholly or partly supported by this program
Feb 1, 2017 – June 30, 2018.

Oral presentations at national and international science meetings

1. Weber, K., Westrop, J., Nolan, J., Bone, S.E., Bargar, J.R., Campbell, K., Snow, D.D. (2018) Microbially-mediated metal/radionuclide oxidation coupled to nitrate reduction in an alluvial aquifer. ACS National Meeting & Exposition, New Orleans, LA, Mar 19. [oral]

2. Bone, S.E., Cahill, M.R., Jones, M.E., Fendorf, S., Davis, J.A., Williams, K.H., Bargar, J.R. (2018) Oxidative uranium release from anoxic sediments under diffusion-limited conditions. ACS National Meeting & Exposition, New Orleans, LA, Mar 20. [oral]

3. Cory, R.M., Trusiak, A., Ward, C., Kling, G.W., Tfaily, M.M., Paša-Tolić, L., Noël, V. and Bargar, J.R. (2017) Interactions between iron and organic matter may influence the fate of permafrost carbon in the Arctic. AGU Fall Meeting, New Orleans, Dec 13. [oral]

4. Bargar, J. R., Noël, V., Bone, S. E., Roycroft, S., Dam, W. L., Johnson, R. H., Williams, K. H. (2017) Redox controls over uranium mobility in hydrologically variable aquifers. Synchrotron Environmental Science Symposium, Brookhaven, NY. [invited]

5. Bargar, J.R., Noël, V.N., Bone, S., Roycroft, S., Williams, K.H., Dam, R. and Johnson R. (2017) Redox, hydrological, and molecular controls over uranium mobility in redox-variable aquifers. Goldschmidt Geochemistry conference, Paris, France, Aug 15, 2017. [keynote]

6. Bargar, J.R., Bone, S.E., Cliff, J., Dynes, J., Janot, N., and Noël, V. (2017) Molecular controls over uranium mobility in complex redox-active sediment systems. ACS National Meeting, San Francisco, CA, April 3. [invited]

7. Bargar, J.R. (2017) SLAC SFA Biogeochemistry Research Program Update. DOE Office of Legacy Management, Grand Junction, CO, Feb 21. [oral]

8. Dublet, G., Lezama-Pacheco, J.S., Bargar, J.R., Fendorf, S., Kumar, N., Lowry, G.V. (2017) Partitioning of Uranyl between Ferrihydrite and Humic Substances at Acidic and Circum-Neutral pH. Goldschmidt Geochemistry conference, Paris, France, Aug, 16, 2017 [oral]

9. Roycroft, S., Noel, V., Boye, K., Johnson, R., Dam, W. L., Fendorf, S., Bargar, J. R., (2018) Vertical transport of uranium in the unsaturated zone: A likely plume persistence mechanism. ACS National Meeting & Exposition, New Orleans, LA, Mar 19-21. [invited]

10. Bargar, J. R., Noël, V., Boye, K., Bobb, C., Cardarelli, E., Kukkadapu, R., Fendorf, S., Maher, K., Francis, C. A. (2018) Iron-sulfur redox cycling and contaminant mobility in the upper Colorad River Basin. Clay Minerals Society 55th Annual Meeting, Urbana-Champaign, IL. [invited]

11. Bargar, J. R., Noël, V., Boye, K., Bobb, C., Cardarelli, E., Fendorf, S., Maher, K., Francis, C. A. (2018) Multi-technique synchrotron investigations of metal and radionuclide behavior in complex biogeochemical systems. 1st National meeting of the Swedish Chemical Society, Lund, Sweden, Jun 20. [keynote]

12. Boye, K., Noël, V., Tfaily, M.M., Schaefer, M.V., Herrmann, A.M., Bargar, J.R., and Fendorf, S. (2018) Implications of microbial energetics for carbon fate in floodplain soils and groundwater. Presented at the DOE ESS PI meeting, Potomac, MD, USA. May 1-2. [invited]

13. Maher K. (2017) Response of hydrologic interfaces to hydrologic fluctuations: the ultimate control on water quality. Gordon Conference on Catchment Science: Interactions of Hydrology, Biology and Geochemistry. Bates College, Lewiston, ME. [keynote]

14. Boye, K., Müehe, M. and Fendorf, S. (2018). Current and future challenges to riceproduction. Presented at the Sustainable Intensification of Agriculture Workshop, Uppsala, Sweden. Jan 30-31. [invited]

15. Stetten, L., Mangeret, A., Seder-Colomina, J., Cazala, C., Brest, J., Othmane, G., Bargar, J. R. and Morin, G. (2017). Uranium scavenging in lake sediments: Importance of mononuclear U(IV) species and ningyoite. TE radionuclides in the environment. Presented at the ICOBTE 2017, Zurich, Switzerland. July 16-20. [oral]

16. Noël, V., Boye, K., Kukkadapu, R., Lezama-Pacheco, J., Fendorf, S., Roycroft, S. J.and Bargar, J. (2017). Fe and S Speciation to Track Redox Constraints on Shallow Alluvial Sediments: Implications for U Storage and Stability. Presented at the Goldschmidt Conference, Paris, France. [oral]

17. Dynes, J., Noel, V., Bone, S. E. and Bargar, J. (2017). Investigation of Organic Matter in Uranium-Enriched Sediments. Presented at the Goldschmidt Conference, Paris, France. [oral]

18. Boye, K., Tfaily, M. M., Herrmann, A. M., Noël, V., Bargar, J. and Fendorf, S.(2017). Carbon in transit – implications of microbial energetics for carbon and contaminant fate in transitory systems. Presented at the SSSA Annual Meeting, Tampa, FL. Oct 22-25. [invited]

Posters presented at national and international science meetings

19. Bargar, J. R., Noël, V., Bone, S. E., Roycroft, S., Dam, W. L., Johnson, R. H., Williams, K. H. (2018) Redox, Hydrological, and Molecular Controls over Uranium Mobility in Redox-Variable Aquifers. Seaborg Institute Science Symposium, Lawrence Livermore National Laboratory, Berkeley, CA. [invited]Roycroft, S., Noël, V., Bargar, J.R., Boye, K., Fendorf, S., Francis, C.A., Maher, K. (2018) SLAC-SFA: Groundwater Quality SFA, Hydrologically driven biogeochemical processes controlling groundwater quality. Presented at the DOE ESS PI meeting, Potomac, MD, USA. May 1-2. [poster]

20. Bobb, C., Maher, K., Boye, K., Noël, V., Bargar, J.R., Dam, W.L, Frazier, W., and Johnson, R.H. (2018) SLAC-SFA: Biogeochemical-Hydrologic Coupling in the Capillary Fringe at the Riverton, WY Site. Presented at the DOE ESS PI meeting, Potomac, MD, USA. May 1-2. [poster]

21. Cardarelli, E.L., Boye, K., Dam, W.L., Bargar, J.R., Francis, C.A. (2018) SLAC-SFA: Groundwater Quality SFA, Microbial niche partitioning at the soil-groundwater interface in transiently reduced floodplains. Presented at the DOE ESS PI meeting, Potomac, MD, USA. May 1-2. [poster]

22. Noël, V., Boye, K., Bargar, J.R., Dewey, C. W., Kukkadapu, R., Tain, Q., Williams, K.H. (2018) SLAC Groundwater Quality SFA: Contaminant response to hydrologic transitions in transiently reduced zones. Presented at the DOE ESS PI meeting, Potomac, MD, USA. May 1-2. [poster]

23. Noël, V., Boye, K., Bone, S. E., Kukkadapu, R., Dynes, J., Lezama-Pacheco, J. S., Cardarelli, E. L., Williams, K. H., Fendorf, S. and Bargar, J. R. (2017). Redox constraints on shallow alluvial sediments: Implications for U mobility. Presented at the 2017 Environmental System Science (ESS) PI Meeting, Potomac, MD. April 25-26. [poster]

24. Müller, A. L., Fendorf, S., Francis, C. A., Bargar, J. R. and Spormann, A. M. (2017). Spatial constraints on microbial metabolic activity in anaerobic environments. Presented at the 2017 Environmental System Science (ESS) PI Meeting, Potomac, MD. April 25-26. [poster]

25. Cardarelli, E. L., Bargar, J. R., Dam, W. L., Johnson, R. H. and Francis, C. A.(2017). Effects of microbial communities on uranium oxidation andmobilization in the presence of nitrate, nitrite, and oxygen. Presented at the2017 Environmental System Science (ESS) PI Meeting, Potomac, MD. April 25-26. [poster]

26. Boye, K., Tfaily, M.M., Herrmann, A. M., Noël, V., Bargar, J.R., Fendorf, S. (2017) Carbon in transit – implications of microbial energetics for carbon and contaminant fate in transitory systems. Presented at Goldschmidt, Paris, France, Aug 13-18. [poster]

27. Boye, K., Noël, V., Bobb, C., Cardarelli, E.L., Dam, W.L., Johnson, R.H., Kukkadapu, R., Tfaily, M., Pasa-Tolic, L., Fendorf, S., Francis, C.A., Maher, K. and Bargar, J.R.(2017) Hydrologically driven process coupling between biogeochemical cycles and solute transport in transiently saturated sediments at the Riverton site (WY). Presented at the 2017 Environmental System Science (ESS) PI Meeting, Potomac, MD., Apr 25-26. [poster]

28. Cardarelli, E.L., Bargar, J.R., Dam, W.L., Johnson, R.H. and Francis, C.A. (2017) Effects of microbial communities on uranium oxidation and mobilization in the presence of nitrate, nitrite, and oxygen. Presented at the 2017 Environmental System Science (ESS) PI Meeting, Potomac, MD., Apr 25-26. [poster]

29. Müller, A.L., Fendorf, S., Francis, C.A., Bargar, J.R. and Spormann, A.M. (2017) Spatial constraints on microbial metabolic activity in anaerobic environments. Presented at the 2017 Environmental System Science (ESS) PI Meeting, Potomac, MD., Apr 25-26. [poster]

30. Noël, V., Boye, K., Bone, S. E., Kukkadapu, R., Dynes, J., Lezama-Pacheco, J.S., Cardarelli, E.L., Williams, K.H., Fendorf, S. and Bargar, J.R. (2017) Redox constraints on shallow alluvial sediments: Implications for U mobility. Presented at the 2017 Environmental System Science (ESS) PI Meeting, Potomac, MD., Apr 25-26. [poster]

31. Dam, William L., Gil, April, Johnson, Raymond H., Campbell, Sam, Bargar, John R. and Picel, Mary. (2017) Long-term stewardship at a former uranium mill tailings site in Riverton, Wyoming - 17090. Presented at the WM2017 Conference, Phoenix, AZ, Mar 5-9. [Poster]