Cover Figure:  A. Baseflow water quality and quantity in rivers and streams is maintained by groundwater discharging into these surface bodies. Groundwater composition (quality) is conditioned by myriad biogeochemical processes along flow routes from source points to surface water. B. Principal biogeochemical functional zones in alluvial systems from surface to deeper: soils, capillary fringe (transiently saturated/reduced), and saturated zone. Water flowing upwards (driven by evapotranspiration and capillary rise) and downwards (driven by gravity) connects biogeochemical function across these zones. C. Biogeochemical reaction networks operating in pore spaces, triggered by hydrological transitions, control groundwater quality by causing organic carbon, nutrients, and contaminants to be filtered out of - or released to – groundwater, and salts to dissolve and precipitate.
Highlights

Coupling between hydrological and biogeochemical processes profoundly influences groundwater quality and biogeochemical watershed function. Spring flooding and high groundwater followed by summer drought (typical of the inter-mountain West) produce intense reducing-oxidizing transitions that trigger changes in microbial metabolic activity, dissolution and re-precipitation of solids, transformations of iron and sulfur, and release/uptake of nutrients and contaminants. While these processes are important to predicting watershed function across scales, we lack quantitative understandings of the thresholds for sediment redox transitions in relation to soil moisture, of the metabolic responses that follow these transitions, and of process rates as controls on groundwater quality responses.

The SLAC Groundwater quality SFA is quantifying and modeling hydrological-biogeochemical processes coupling in alluvial sediments, from bedrock to surface in order to understand the molecular-scale reaction networks that control groundwater quality. We are studying how hydrology impacts biogeochemical function by triggering and sustaining thermodynamic disequilibrium (including “hot spots/moments”), how soil moisture triggers these conditions, and how to represent these systems in quantitative model frameworks. Our program is organized around four subtasks that link hydrology to biogeochemical function and water quality: 1) the rhizosphere, 2) reduced zones, 3) the shallow aquifer, and 4) transformations and transport of reactive solids.

Our research is strategically advancing BER’s Biogeochemistry Scientific Grand Challenge by:

• Understanding how geochemical, genomic, and metabolic interactions influence watershed function
• Improving our ability to predict biogeochemical function under perturbation
• Advancing our understanding of thresholds for and sustenance of hot spots and hot moments.

Accomplishments. We made tremendous progress in the past year addressing major scientific questions and making several important discoveries. We published 8 papers, submitted 2 manuscripts (currently in review), and presented 19 talks (1 keynote, 12 invited) and 8 posters.

1. Which factor has the largest impact microbial communities in wet-dry/redox-cycled aquifers; depth of burial, or seasonal moisture? DNA sequencing at the Riverton site shows that microbial community composition was most strongly controlled by depth and the physico-chemistry of sediment horizon, and exhibited relatively little response to large seasonal changes in soil moisture, temperature, and pore water chemistry (Tolar et al. in prep). This insensitivity is surprising and suggests that the dramatic seasonal transitions from oxic to reducing conditions neither eliminate niches for community members nor are caused by major regime shifts in the microbial community. Rather, it is likely that redox transitions are driven by only a small fraction of the microorganisms. Moreover, these findings underscore the likely importance of microsites in maintaining community structure and function.

2. Do naturally reduced zones (NRZs) create biogeochemical “shadows” that influence the surrounding aquifer? A column experiment performed in the past year demonstrated that NRZs do indeed spread reducing conditions into the surrounding aquifer, increasing microbial activity and sulfidizing sediments (Kumar et al. in prep, Boye et al. in prep). We found that NRZs profoundly influenced downgradient groundwater quality, and in particular Fe, S, and U behavior was strongly modified in the column system (representative of the Riverton aquifer). For example, uranium was exported from NRZs likely as organically complexed U(IV) and retained in aquifer sand. Our measurements underscore the role of NRZs in maintaining aquifer nutrient supply and redox status.

3. Modeling shows how redox fluctuations lead to accumulation of U. Centimeter-scale reactive transport simulations of elemental cycling across aquifer-NRZ interfaces under Riverton conditions
suggests that diffusion into organic enriched, water saturated sediments limits the remobilization and release of U during seasonal oxygenation events, leading to an overall accumulation of U inside NRZs over geochemical cycles.

4. Colloids mobilize Fe, S, and metal mobilization in Slate River floodplains. Groundwater sampling in 2018 revealed that a large fraction of total “aqueous” Fe, S, and metals in the saturated zone our Slate River floodplain study site are in fact, associated with colloids. Based on the relatively high abundances of Fe and S in the colloids and their affinity for chalcophile (sulfide-seeking) elements (e.g., Zn), we believe the colloids are FeS nanoclusters (cf., next highlight). This finding opens the door to understanding influences of colloids on nutrient and contaminant transport.

5. What controls colloid generation and mobility in wet-dry cycled alluvium? Our 2018 experimental program simulated reductive dissolution of FeIII-(oxyhydr)oxides by HS-, an important process in NRZs. We found that mackinawite (FeS) nanoclusters were produced that were stable in solution. While sulfide nanoparticles have been reported, no theoretical framework has been advanced to rationalize and predict when and why stable colloids are produced. Here, we have shown colloid stability is controlled by the type of organic matter, ionic strength, and sulfidation rate are major controls (Kumar et al., (2018; in prep)11; Noël et al. (in prep., a & b)13,14; Trusiak et al., (in prep.)16. These results represent a major advancement that impact the broad biogeochemistry community.

6. Sensor development and implementation. We tested a suite of in-situ solute and gas sensors to identify which brands, models and sensor types will be most durable, precise and reliable. Based on the results of this evaluation program, we are installing sensor arrays at our Riverton and Slate River sites for continuous monitoring of subsurface parameters. We further engaged in a SBIR-supported collaborative partnership to help QBI, inc. to develop microbial sensors for N species and metals.

1. Program overview

Groundwater quality is enormously important to water security as frequent drought, increased temperatures, and growing populations erode and overwhelm the capacity of surface water supplies. Changes in sediment moisture profoundly influence biogeochemical processes, groundwater quality, and watershed function. Moreover, groundwater discharging at the landscape surface maintains flow and quality of river water at base conditions. Thus, the hydro-biogeochemical processes that maintain groundwater quality also serve to maintain surface water quality.

Redox transitions are profoundly important to watershed function. Few terrestrial environments are more emblematic of, and influenced by, groundwater level fluctuations and ensuing redox transitions than
alluvial floodplains, experiencing seasonal and episodic drought and flooding oscillations (Cover figure). Microbial metabolic activity associated with redox transitions transforms carbon, nutrients, minerals, and contaminants and alters their susceptibility to transport\textsuperscript{1,17,18,19}. It is generally understood that redox transitions are triggered by changes in sediment moisture and moderated by parameters that regulate oxygen supply and demand, such as organic matter concentration and permeability\textsuperscript{1,21}. Crucially, however, we lack qualitative and quantitative understanding of thresholds for redox transformations in relation to soil moisture, metabolic responses, and process rates. This gap reflects numerous underlying deficiencies in our knowledge of biogeochemical reaction networks, creating uncertainty and preventing us from accurately capturing these systems in numerical models. Yet, without such knowledge, we cannot link water quality to biogeochemical, redox, and water cycles.

The mission of the SLAC Groundwater Quality SFA is to create penetrating new knowledge of processes controlling groundwater quality to help encode knowledge into conceptual and numerical models so it can be utilized to safeguard national water and energy security.

Central scientific question: We are addressing the question: How do biogeochemical and hydrological processes in alluvial groundwater systems (bedrock to rhizosphere) couple to one-another and mediate biogeochemical function and water quality under hydrologically variable conditions?

Approach: We are performing research to experimentally interrogate and model the coupling of hydrological and biogeochemical processes in shallow alluvial systems impacted by mining and ore processing activities. 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. In order to test hypotheses developed from our biogeochemical functional zone model (Cover figure), we are conducting groundwater sampling activities at two sites, Riverton, WY and Slate River, CO sites. The two sites are necessary to test hypotheses that address contrasting geochemical and climate conditions (Riverton: 5,000 ft elevation, higher-salinity groundwater with low colloid mobility vs Slate River: 9,500 feet elevation, low-salinity groundwater, and high colloid mobility). The sites also allow us identify transport and hydrological-biogeochemical processes that have high similarity between across sites, e.g., ET-drive upward transport of solutes, such as sulfate and dissolved oxygen. Insights from each location accelerate evaluation and discovery of processes at the other site.

Importance of synchrotron techniques. Synchrotron X-ray imaging capabilities at SSRL provide powerful capabilities to image solute transport and biogeochemical reactions occurring within soil matrices that are not accessible to electron, Raman, and fluorescence/light microscopy, which cannot penetrate intro the soil matrix. X-ray absorption spectroscopy is crucial to quantifying the chemical form of sulfur, iron, and other important water quality solutes.

Importance of external collaborations. We are collaborating with C. Varadharajan and J. Damerow (LBNL) and J. Stegen (PNNL SFA) to help develop BER database and community science tools. We are collaborating with N. Cookson (QBI, Inc) to develop microbially-based sensors for dissolved N species and dissolved metals. We also are collaborating with external groups through cooperative arrangements and scientific user facility proposals (cf. section 4.d.) to provide expertise complementary to our team, including ultra-high resolution mass spectrometry, Mössbauer spectroscopy, isotope nano-imaging, trace gas flux analysis, rhizosphere dynamics, Fe-organic colloid chemistry, and trace metal colloid transport. Our collaborative publications (Appendix A) reflect this activity.

Impact and relevance to BER: Quantitative process representations and reaction networks produced by this program will advance BER toward its Biogeochemistry Scientific Grand Challenge goals. We are providing new models to understand thresholds for redox transitions and nutrient/micronutrient/contaminant mobilization in relation to soil moisture, metabolic responses, and process rates.
2. Outline of scientific objectives

We are focusing on four subtasks, each linking hydrology to biogeochemistry and water quality through process and numerical modeling: 1) the rhizosphere, 2) reduced zones, 3) groundwater, and 4) contaminant-controlling processes.

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 Groundwater Quality 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 embedded within SSRL provides members of the Groundwater Quality SFA intimate contact with synchrotron methodological capabilities, developments, and expertise. Our staff contributes to SSRL strategic planning and instrument development, which in turn helps to maintain beam line facilities in a state of readiness for biogeochemistry research needs.

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

Relationship with Stanford University. The Groundwater Quality SFA benefits tremendously from our proximity to Stanford University. This connection helps us to attract and retain the best and brightest students and postdoctoral researchers from around the World. 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 (soil, solute, and gas quantification), and Stanford nano-shared facilities.

Communications. Our group meets twice-monthly to 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. This is supplemented by frequent ad-hoc small-group meetings and less frequent leadership-group meetings.

Mentoring tomorrow’s scientific workforce. We encourage postdoctorals and students to provide program leadership and to build skills needed to become strong independent scientists, particularly developing strong organizational, communication, mentoring, and networking skills. We emphasize publishing papers, presenting results at scientific meetings, organizing symposia, writing and reviewing proposals, and participating in field work and modeling activities.

4. Performance milestones and metrics toward accomplishing 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.

Table 1. Summary of FY2019 program and goals for FY2020. Grey text corresponds to subtasks which were not scheduled to be active in FY2019.

<table>
<thead>
<tr>
<th>Hypotheses</th>
<th>FY19 goal</th>
<th>Status</th>
<th>Pages in report</th>
<th>Deliverables</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Subtask 1. Influence of rhizosphere processes on carbon dynamics and contaminant-hosting phases</strong></td>
<td></td>
<td></td>
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<tr>
<td>Hypothesis 1.1. Root presence increases the rate of formation and abundance of mineral precipitates in capillary fringe conditions</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>1.1.a. Roots increase evaporite mineral precipitates</td>
<td>Initiate rhizobox experiment</td>
<td>In progress</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>1.1.b. Roots modify types of evaporite mineral precipitates</td>
<td>Initiate rhizobox experiment</td>
<td>In progress</td>
<td>NA</td>
<td>NA</td>
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<tr>
<td>Hypothesis 1.2. Roots modify the types of minerals that form in response to changing water saturation</td>
<td></td>
<td></td>
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<tr>
<td>Hypothesis 1.3. Export of plant derived C from the rhizosphere is dominated by CO$_2$ and dissolved inorganic C$_2$ Decomposition products from soil organic matter and colloids dominate the export of organic C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.3.a. Plant derived C exported from rhizosphere is dominantly inorganic</td>
<td>Starting FY20</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>1.3.b. Organic C export from rhizosphere is dominantly from SOM</td>
<td>Starting FY20</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
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<tr>
<td><strong>Subtask 2. Biogeochemical redox responses to hydrological transitions</strong></td>
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</tr>
<tr>
<td>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</td>
<td>Field sampling</td>
<td>In progress</td>
<td>9-10</td>
<td>This report \ Pie meeting posters</td>
</tr>
<tr>
<td>Modeling Task 2.2. Reaction network modeling of TRZ sediment Fe/S redox cycles.</td>
<td>Field sampling</td>
<td>In progress</td>
<td>9-10</td>
<td>This report \ PI meeting posters</td>
</tr>
<tr>
<td>Hypothesis 2.3 TRZ sediments will exhibit large-scale shifts in dominant functional guilds corresponding to oxic (unsaturated) vs. reducing (saturated) conditions</td>
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<tr>
<td>2.3.a. Nitrifiers will be most abundant and active under oxic conditions, dropping off rapidly as conditions become anoxic and especially sulfidic.</td>
<td>Sequencing \ Data Analysis</td>
<td>In progress</td>
<td>8-9</td>
<td>This report \ Manuscript 7 (Appendix A) \ PI meeting poster \ Scientific talks</td>
</tr>
<tr>
<td>2.3.b In the presence of trace sulfide, nitrate-reducing communities will be partially inhibited by Mo limitation.</td>
<td>Conduct column experiment</td>
<td>In progress</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Subtask 3. Impacts of hydrological-biogeochemical coupling for solute transport and groundwater biogeochemistry</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1 NRZs dominate contaminant sequestration and nutrient release to GW during the dry season and when infiltration is limited</td>
<td>Publish manuscript</td>
<td>In progress</td>
<td>10-11</td>
<td>This report \ Manuscripts 8, 10 \ Posters at SSSA and PI meetings \ Scientific talks</td>
</tr>
<tr>
<td>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</td>
<td>Initiate pilot experiments</td>
<td>In progress</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>
3.3 Rapid snow melt of floodwater infiltration leads to oxidative release and evaporate dissolution, releasing salts and contaminants and impacting the entire aquifer

Modeling Task 3.4. Reactive transport modeling; advective coupling of TRZs and underlying saturated zone

| 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 |

| Task 4.3 Reaction network modeling; impact of TRZ Fe/S redox cycles on contaminant release (coincident w/ Modeling Task 2.2) |

| In FY2019, the Groundwater Quality SFA focused on executing several major new activities proscribed in our project management plan (Table 1), including: reactive transport modeling and genomic analysis of samples collected at the Riverton, WY site in summer 2018 (Tasks 2), a major laboratory column experiment (Task 3), a field sampling campaign at Slate River, CO, and subsequent sediment and pore water analyses and a major laboratory study of sulfide colloid generation and stabilization mechanisms (Task 4). Genomic and spectroscopic analyses were performed under a FICUS proposal at JGI and EMSL. Two new SSRL user facility proposals were submitted and subsequently funded with good scores, and 10 manuscripts were published or submitted for publication. Over the next 12 months, we will focus on collecting samples at both the Riverton, WY and Slate River, CO sites as needed to address our goals (Table 1). 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), 2.3.b (Mo effect on nitrate reducers), 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 well as Pb (Subtask 4.2.c), Zn (Subtask 4.2.d), and Mo (Subtask 4.2.e). As these activities complete, we plan to initiate experimental activity in Subtask 1.1 (impact of roots on mineral precipitates) and Subtask 3.2 (infiltration associated with rain events). We will also focus on completing and submitting manuscripts in progress.

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 just ramping up with a pilot rhizobox experiment currently running, and a full experiment addressing hypotheses 1.1a and 1.1b being started in Sep 20.


Seasonal changes in microbial community. (Hyp. 2.3) B. Tolar (lead), E. Cardarelli, K. Boye, J.R. Bargar, C. Francis. The consequences of intense, intermittent hydrological transitions on biogeochemistry are largely governed by the microbial response. Yet, the connection between microbial and geochemical processes is not well understood, especially in heterogeneous, non-steady state systems.

We sought to illuminate these connections by focusing on a single area at the Riverton site, sampled monthly from April to September 2017, to capture both wet and dry conditions. We extracted and sequenced DNA from all samples and found that soil horizon (near-equivalent to sample depth) is the primary driver of microbial community composition. However, small changes at the microbial phylum level could be observed within a single soil horizon over time, with the most noticeable differences occurring after a rain or flooding event (Figure 1). Geochemical data collected from the same samples showed similar patterns of clustering by soil horizon, with a clear distinction between upper (seasonally saturated) and lower (consistently saturated) soil depths. Soil

Figure 1. Phylum-level barplot of all taxa sequenced, clustered by soil horizon and separated out by sampling month. The most striking differences can be observed before (May) and after (July) the flood event in June 2017.
moisture thus played a role in determining community structure in our dataset and may impact specific taxa. Additionally, members of the deltaproteobacteria were connected to increased concentrations of U, Mo, and Fe. This is especially intriguing, as we have observed an increase in U mobilization after flood events, where we also see changes in the microbial community. As part of a collaboration with JGI, these connections will be further investigated using metagenomics and metatranscriptomics, where we hope to assess the impact these taxa may have on mobilization of metal contaminants at Riverton.

**Impact:** Our findings thus far indicate that microbial communities are generally stable during seasonal change, indicating resilience to fluctuating redox conditions. However, community changes within specific soil horizons indicate that soil moisture plays a key role and may indicate that ‘hot moments’ are occurring during seasonal transitions with significant impacts on microbial metabolic activity. Continued investigations into the metabolic potential and activity of microbes can elucidate specific connections between microbial activity and groundwater quality at Riverton.

**Modeling of NRZs indicates that redox fluctuations lead to accumulation of U.** (Modeling tasks 2.1, and 2.2) T. Babey (lead), Z. Perzan, C. Bobb, K. Boye, J.R. Bargar, K. Maher. We developed a reactive transport model to characterize the capacity of NRZs to exchange solutes with the surrounding aquifer. Numerical experiments were carried out at the cm scale in water saturated conditions, using the numerical code CrunchFlow, explicitly accounting for C, Fe, S and U cycling across NRZs-aquifer interfaces. We considered simplified NRZ geometries (Figure 2) and geochemical cycles similar to conditions at the Riverton site. The simulations show a net accumulation of reduced U inside the NRZ, with limited remobilization during oxygenation events (about 10% of total stored U). Oxygen penetration inside NRZs is limited to only the first few cm from the aquifer-NRZ interface, even during aquifer oxygenation events such as occurs during snowmelt. When NRZs are \( \geq 5 \) cm thick, some of the remobilized U(VI) can

![Figure 2](image_url)
diffuse from the external layer into - and become trapped within - the reduced interior of the NRZs, preventing any future release.

**Impact:** The simulations emphasize the importance of diffusion in limiting exchanges between fine-grained NRZs and the aquifer. Under water saturated conditions, NRZs are likely to act as sinks rather than secondary sources for redox-sensitive contaminants like U, due to limited remobilization during oxygenation events. Large seasonal shifts in U storage would instead require additional physical or biogeochemical processes, like partial drying of the sediments that allow oxygen to penetrate more deeply into the interior of the NRZs.

**Subtask 3. Impact of hydrological-biogeochemical coupling on solute transport and groundwater biogeochemistry. S. Fendorf (lead)**

**Dominance of NRZs on groundwater chemistry during baseflow conditions.** (Hyp. 3.1 & 3.3) K. Boye (lead), N. Kumar, V. Noël., J.R. Bargar, S. Fendorf. The heterogeneity of floodplain aquifers, due to varying organic matter composition, texture, and mineralogy, leads to the establishment of naturally reduced zones (NRZs) in otherwise dominantly oxic/suboxic aquifers. It has been postulated that NRZs have a strong influence on groundwater chemistry and are responsible for the alternating release/retention of contaminants in response to oxygenation of groundwater. To determine the magnitude of NRZ influence on aquifer chemistry, we conducted a dual domain column experiment, where varying numbers of fine-grained, organic rich lenses (i.e. NRZ analogues), containing elevated uranium concentrations and a natural abundance of arsenic and sulfide, were deposited within a coarse-grained aquifer material from the Riverton field site. Oxygenated groundwater was pumped through the columns and depth resolved pore-water data was collected from inside sulfidic zones and between them. Contrary to prevalent hypotheses (but supporting recent findings\textsuperscript{23}) that reduced zones release oxidation-sensitive contaminants, such as uranium, when exposed to aerated groundwater, our results show no indications of oxidation inside the NRZ analogues. Instead, we observed that the reducing conditions spread into the coarse-grained aquifer material. The diffusion of sulfide into the groundwater was accompanied with a mass transfer of uranium (presumably in its reduced form, transported as organo-complexes), organic carbon, and reactive Fe(II) (HCl-extractable) to the primary aquifer solids. Notably, about 20% of the initial organic matter was lost from the NRZs during the 10 week long experiment, with almost equal amounts lost to respiration, DOC outflow, and transfer to aquifer solids. Arsenic behaved oppositely to U, Fe(II), and C, and moved from the aquifer sand into the clay lenses. Importantly, our results show that aqueous iron to sulfide ratios regulate arsenic mobility (Figure 3) and speciation; slightly sulfidic groundwater can contain toxic levels of arsenic (due to thiolation of aqueous arsenic) even if sediment arsenic concentrations are low.

**Impact:** These results highlight the importance of redox interfaces for controlling contaminant behavior.
in groundwater and suggest reducing conditions may spread from fine grained, organic rich lenses even within an aerated primary aquifer. Our findings have implications for groundwater quality at a spatial scale smaller than normally resolved and may offer explanations for locally deviant behavior of contaminants from predictions based on large-scale sediment composition analyses.

Subtask 4. Mechanisms controlling release/uptake of nutrients and contaminants. J.R. Bargar (lead)

*Slate River floodplain water quality response to seasonal drought and wet-up.* (Hyp. 4.1 and 4.2) J.R. Bargar (lead), C. Dewey, K. Maher, and K.H. Williams (LBNL). Throughout summer 2018, we sampled pore water at two floodplain locations along Slate River, CO, to provide comprehensive temporal and spatial data on groundwater solute concentrations, reactive alluvium phases, and microbial community dynamics. Similar solute dynamics were observed at both sites. Here we focus on site OBJ2, for which there are more data. We were able to resolve three hydro-biogeochemical stages:

i. *June: Falling water table and drought.* In the **transiently saturated zone** (30-100 cm), dissolved sulfate (total dissolved S) was elevated (≤ 0.3 mM) while Fe was low (<0.7 mM), suggesting that (sub-)oxic conditions were present (Figure 4). In the **saturated zone** (< 100 cm), sulfate concentrations exhibited their lowest values (<0.16 mM) but Fe was elevated (< 3.6 mM), indicating that reducing conditions were present. The persistence of these solutes despite the falling WT can be ascribed to the tendency of the clayey sediments to slowly lose moisture.

ii. *July - early August: Base flow.* Depth-averaged concentrations of sulfate and Fe, as well as Ca dropped (Figure 4) by factors of 8.6, 10.7, and 9.8, respectively, between July 2 and Aug 7. The similar **timing and extents of loss**, irrespective of their depth, suggests that these solutes were diluted or displaced by lower-conductance water, presumably from infiltrating rainfall (since the WT dropped during this period). The site did receive above-average rainfall during July, two-thirds of which fell in a single event 9 days before sampling in Aug, which could have caused dilution or flushing. Iron likely also was lost due to oxidation of soluble Fe(II) to insoluble Fe(III), consistent with the fact that iron exhibited the largest apparent loss factor. However, it is difficult to ascribe wholesale Fe loss at 130 cm depth to onset of oxidizing conditions because: (a) 130 cm was always below the WT (air did not enter), and (b) XANES analyses (not shown) indicate that mackinawite (FeS), which is rapidly oxidized by O₂, was present at this depth in August.

iii. *Late Aug-Oct: Wet-up.* 2 in of rain fell between Aug 7 and Sept 11. Dissolved Fe and sulfate remained low. Mackinawite was observed below 110 cm, suggesting that reducing conditions persisted.

**Zn solid-phase speciation and behavior:** X-ray microprobe imaging and preliminary X-ray absorption spectroscopy analyses show that zinc is associated with sphalerite (ZnS) and clays in the saturated zone. At shallower depths, sphalerite is less abundant, and Zn is also associated with a host believed to be iron oxide. Thus, multiple hosts are present for Zn. In contrast, sulfate will be weakly sorbed at the soil
solution pH (6.3). However, oxidative dissolution of sulfides in the presence of oxygen is expected to release Zn to solution.

Between June 5 and August 7, dissolved Zn increased in pore water, with the greatest accumulation (4-fold) occurring during base flow at a depth of 90 cm, *i.e.*, just above the WT. Zn concentrations increased *despite likely dilution or flushing* in July, suggesting that overall release was robust. It is plausible that Zn was released due to sulfide oxidation as the WT fell and air permeated into sediments. Zn decreased sharply between Aug 7 and Sept 11 and remained low in Oct. This loss could be due to downward transport during the weaker-than-normal monsoonal rains in Aug, or potentially through a chemical by precipitating Fe oxides. In any case, the rate of Zn release slowed in Aug. We are performing sequential extractions to constrain Zn host identities and better understand this behavior.

*Solute transport by colloids:* Sequential size filtration showed that colloids (> 20 nm diameter) are mobile in the floodplain aquifer. Remarkably, they contained *half* of total “aqueous” Zn, S, and C and *two thirds* of “aqueous” Fe, indicating that colloids are important to nutrient and contaminant transport at this site. Based on our laboratory findings, we posit that these colloids are mackinawite nanoparticles. We are systematically sampling groundwater in 2019 to better understand conditions under which colloids form.

*Figure 5.* Conceptual model of Slate River alluvial stratigraphy and impact of vertical transport on biogeochemical processes and water quality. Fine-grained organic-enriched sediments overlay hydraulically conductive cobble aquifer. A. Rainfall and snowmelt infiltration drive downward transport, whereas evapotranspiration (ET) drives upward transport of dissolved oxygen from the cobble layer into overlying sulfidic fine-grained sediments. Conversely, groundwater discharging downward from alluvium can carry dissolved and colloidal zinc into the cobble-river system. B. Sulfide oxidation releases Zn into porewater.

**Impact of vertical transport on water quality.** The solute trends noted above suggest that gravity-driven downward flow of water, coupled with biogeochemical activity, has a large impact on a range of water quality solutes. We also have observed evidence for *upward* flow of water. Key observations include: (i) nightly water table rise of *ca* 5 cm (data not shown) during the growing season, and (ii) Fe solute data *(Figure 4)* from 150 cm depth. Fe concentrations *decrease* moving down-profile to this depth, suggesting that Fe(II) was oxidatively consumed by O$_2$ that had diffused up from the immediately underlying hydraulically conductive cobble layer at 160 cm *(Figure 5)*. During the 2019 field season, we will use specific conductance profiles to observe water flow directions across the fine-grained/cobble interface and correlate them with vertical hydraulic head and solute concentration changes.

**Impact:** Robust vertical transport and biogeochemical activity drive large swings in groundwater quality and likely drive both export and import of solutes from the river-cobble aquifer system.

**Colloid formation and stability during sulfidation.** *(Hyp. 4.2) V. Noël (lead), N. Kumar, K. Boye, J.R. Bargar.* Sediment-water interactions driven by biogeochemical processes are important mediators of metals and radionuclides, governing their storage and behavior in soils, sediments, and aquatic systems. In this context, the generation of colloids (submicron-sized mineral particles or organic matter that remain
in suspension and move with the aqueous phase) are suspected of mediating the mobility of metals, actinides, and nutrients in sediments that experience strong wet-dry cycling, and subsequently impact the groundwater quality. Sulfidation processes have been proposed to generate sulfide colloids, however direct evidence for their formation is still lacking. Improved knowledge of the nature of colloids and parameters controlling their generation and metal(loid) binding is critically needed to improve our understanding of water quality responses to hydrological changes. In this study, we hypothesized that, during hydrologically induced redox transitions, oxidation of dissolved sulfides (onset of oxidizing conditions) or reductive dissolution of goethite and ferricydrite (reducing conditions), releases organic carbon, metals, and anions, providing conditions ideal to generate colloids that can bind and mobilize metal(loid)s, such as Zn, Pb, and U.

Figure 6. Sulfide colloids (FeS) generated during sulfidation of OM-ferricydrite aggregates. Their residence time in suspension is correlated to S/Fe ratio. Low sulfidation (S/Fe ≤0.5): FeS remain stable in groundwater at least 14 days; High sulfidation (S/Fe >0.5): promotes aggregation of FeS colloids.

Here, we examined the influence of sulfidation of FeIII-(oxyhydr)oxide nanoparticles associated with organic ligands on the generation, stability, and nature of colloids. We observed that reductive dissolution of ferricydrite\(^8\) (proxy of goethite) generated nanoclusters of mackinawite (FeS; Figure 6). Their subsequent aggregation, which promotes settling of mackinawite into the solid phase, was directly correlated to the concentration of sulfides relative to iron oxides (S/Fe ratio). At low sulfide concentration (S/Fe ratio ≤0.5), the aggregation of mackinawite nanoclusters took between 14 days to 2 months, indicating that colloids generated from sulfidation are able to bind and transport metals in groundwater for at least 14 days after their generation. Inversely, at high sulfide concentration (S/Fe ratio >0.5) the sulfidation rate was rapid and the aggregation of mackinawite nanoclusters was accelerated. This inhibited the generation of suspended FeS colloids. However, the S/Fe ratio also controlled the concentration of DOC, which dramatically increased at high sulfide concentrations, thus promoting the mobility of organic-bound metals at conditions when FeS colloids were insignificant. Finally, the presence of organic ligands increased the time of suspension of mackinawite nanoclusters, whereas an increased ionic strength of the groundwater inhibited the generation of FeS colloids.

Our first investigation in the field and simulation experiment in laboratory confirms our observations:

- Slate River (CO) within the LBNL Watershed Function SFA study area – characterized by low S/Fe and low ionic strength groundwater: the porewater collected in the alluvium saturated zone of Slate River suggest that a large fraction of DOC occurs concomitantly with iron sulfide colloids. Porewater
Pb and Zn distribution, important alluvial contaminants at Slate River, seems correlated with the presence of DOC and FeS colloids.

- Riverton, WY DOE legacy ore processing site – *characterized by high S/Fe and high ionic strength groundwater*: the simulation experiment of Riverton geochemical condition show that porewaters are enriched in DOC but no FeS colloids have been detected. Furthermore, a considerable part of U released during sulfidation of U-sorbed OM-ferrihydrite bind with DOC and stay suspended in water.

**Impact:** Our experimental results show that colloids formed during sulfidation of OM-ferrihydrite aggregates can mobilize contaminants in two ways:

- **At low sulfidation (S/Fe ≤ 0.5) and low ionic strength:** production of stable FeS colloids promotes the mobility of FeS-associated contaminants;
- **At high sulfidation (S/Fe > 0.5) regardless the ionic strength:** FeS colloids are not stable, but DOC is released, promoting the mobility of organic-bound metals.

These results are providing a framework of reaction rates and products dependent on the stoichiometric composition of solid and aqueous phases, which will be crucial for including colloidal transport of contaminants in reactive transport models for alluvial groundwater. This investigation provides, for the first time, a general conceptual model to predict the formation of sulfidic nanoparticles, which has relevance to the wider geochemical community.

**Organic matter complexes control uranium mobility in anoxic sediments.** S.E. Bone (lead), J. Cliff (EMSL), S. Roycroft, M.R. Cahill, S. Fendorf, J.R. Bargar. Uranium occurs naturally in alluvial sediments, where it accumulates as tetravalent U [U(IV)]. It is generally understood that fluctuating hydrologic and geochemical conditions cause U(IV) to be released into groundwater. However, the geochemical mechanisms by which uranium is released remain unknown. There is growing belief that soil-associated organic compounds bind U(IV) - a form once considered largely immobile - and mediate its fate in the subsurface. In this work, we combined nano-scale imaging (nano secondary ion mass spectrometry and scanning transmission X-ray microscopy) with a density-based fractionation approach to physically and microscopically isolate organic and mineral matter from natural alluvial sediments contaminated with uranium. In the past year we extended and deepened our analyses of these data, leading to the identification of two distinct populations of complexed U control its behavior in anoxic sediments: (i) U adsorbed to organic matter (including particles rich in both carboxylate and phenolic functional groups) and (ii) U adsorbed to organic-clay aggregates. This is the first study to demonstrate unambiguously a major role for organic matter as a U(IV) sorbent in unaltered sediments from an alluvial aquifer.

![Figure 7: Model for U(IV) speciation (A) and mobilization from anoxic sediments (B).](image)

U(VI) diffuses into anoxic fine-grained clayey/organic-enriched sediments, where it is reduced and accumulates as U(IV) complexed to sediment organic matter and clay-organic aggregates. (A). Changes in alkalinity (typically dominated by bicarbonate ion), ionic strength (ΔI), redox potential (ΔEh) and pH occur during inundation or drying periods. (B). When exposed to changing geochemical conditions, U(IV) can be mobilized by desorption, complexation, and colloid mobilization, in addition to oxidation. Mobilized U(IV) is highly susceptible to oxidation during transport.
Impact: Previously, oxidation of U(IV) has been posited as the dominant mechanism by which U is released into groundwater. However, depending on the redox-buffering capacity of the sediment, U(IV) can persist during influxes of oxidants, such as \( \text{O}_2 \) and \( \text{NO}_3^{-} \). An additional mechanism of U mobilization from anoxic sediments is therefore needed to explain persistent elevated groundwater concentrations. We suggest two possibilities, illustrated in Figure 7. First, adsorbed U(IV), whether complexed by organic matter or clay mineral surfaces, could be mobilized by desorption; in particular, by \( \text{HCO}_3^{-}/\text{CO}_3^{2-} \), which solubilizes non-mineral forms of U(IV). This is consistent with recent work, which has connected an increase in total inorganic carbon in groundwater to elevated groundwater U concentrations. Second, our work provides a mechanistic context for colloidal mobilization of U(IV). We speculate that U associated with POC could be mobilized as that POC is transformed into smaller, more oxidized and more soluble units through hydrolytic degradation reactions. Organo-mineral aggregates also are subject to disaggregation under changing geochemical conditions, causing the release of organic matter into the dissolved and colloidal phase, along with associated metals. Once mobilized through complexation by \( \text{HCO}_3^{-}/\text{CO}_3^{2-} \) or colloidal organic matter, U(IV) could be transported into oxygenated zones where it could then be oxidized to U(VI). Thus, we conclude that the dominance of OM-associated U provides a new framework to understand U mobility in the subsurface.

An unforeseen pathway of U(VI) reduction by Fe(II) resulting in U(V). C. Dewey, J.R. Bargar, and S. Fendorf (lead). Understanding U reduction pathways, and the mechanisms promoting or inhibiting these pathways, is essential for understanding the controls on U solubility, and therefore U transport and its associated risks. We used U L\( _3 \) XANES, EXAFS, and TEM to uncover an unforeseen pathway of U(VI) reduction by Fe(II)\( _{\text{aq}} \), resulting in the incorporated of U(V) into ferrihydrite. Through a series of kinetic experiments in which we varied the initial proportion of calcium uranyl carbonato species, CaUO\(_2\)(CO\(_3\))\(_2^{2-} \) and Ca\(_2\)UO\(_2\)(CO\(_3\))\(_3\), we found that the overall rate of U(VI) reduction by Fe(II)\( _{\text{aq}} \) decreases as U speciation shifts towards a higher proportion of calcium uranyl carbonato species, resulting in a greater proportion of soluble U. We also found that reduction of the calcium uranyl carbonato species by Fe(II) proceeds when ferrihydrite is present, but does not proceed in a homogeneous system.

Impact: Reduction of calcium uranyl carbonato species by surface-bound Fe(II) is unimpeded and likely to be a dominant water quality-controlling reaction in watersheds.

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

An ultimate goal of this SFA program is to understand and characterize what molecular reactions/processes are most important to water quality and watershed function. In order to answer this question, we must also determine when and where specific reactions or reaction networks occur within the hydrologically active portion of the landscape (i.e., where water quality reactions occur). Here we describe a vision for two new activities that will address these key questions, that we intend to propose in FY 2020 as part of our Science Plan renewal. The new activities will share resources and strongly reinforce one-another, yet are independent and can proceed in parallel. Data from the Real-time sensor technology and groundwater quality modeling activity will inform interpretation of aerial imagery in the Surface signatures activity, thus improving the “segmenting” of landscape features indicative of specific subsurface processes. Similarly, the Surface signatures activity will provide information on optimal locations for placement of new real-time sensor arrays. Moreover, hybrid data science models (developed in the real-time sensor technology and modeling activity) will provide new abilities to integrate diverse data streams, from molecular to remote sensing. Both activities will leverage our scientific and infrastructure advancements in the past 2 years. Both will robustly advance CESD strategic goals.
Using new real-time sensor technology to advance groundwater quality modeling. Transient hydrological events, such as flooding and monsoonal rainfall, that drive dissolved solutes through the subsurface are often rapid (minutes to weeks) but are profoundly important to biogeochemical function and groundwater quality. Upward fluxes of nutrients and solutes due to evapotranspiration and capillary rise are equally important and rapid (hours to weeks).

Challenge: It is not possible to measure or predict transient biogeochemical responses to rapid hydrological forcing using discrete sampling events (e.g., typically weekly or monthly), which is the current best practice. Consequently, modeling biogeochemical responses to environmental change remains an outstanding challenge. To our knowledge, this problem has not been solved and is an important technical challenge for all of the CESD-funded national lab programs.

Opportunity: Recent advances in data science and in-situ solute sensor technology – when combined with robust biogeochemical models – offer a unique opportunity to address this challenge. Over the past several years, improved computing power and the availability of large datasets have driven an explosion in the use of data science approaches (e.g., machine learning, especially deep learning, information theory, Kalman filtering) in the broader scientific community. Meanwhile, application of new algorithms in subsurface and biogeochemical science has lagged behind, partly due to insufficient data. Networks of in situ environmental sensors offer a first step in bridging this gap, providing continuous, high frequency measurements of hydrologic conditions, microbial metabolic activity and key biogeochemical constituents. Unfortunately, sensor data alone is likely inadequate to build a predictive biogeochemical understanding, requiring that the sensor data be coupled with traditional physics-based models, such as IDEAS reactive transport models (RTMs). In addition, in spite of ongoing advancements, modern sensors measure only a small subset of components in the complex microbial and geochemical reaction networks that contribute to groundwater quality and existing model RTM frameworks tend to be fairly rigid in terms of the types of data streams they can ingest whereas data science approaches are far more flexible. A hybrid data science approach, that learns from both the sensor network and RTMs, may lead to new insights into processes, and ultimately to true tests of predictive understanding.

We envision that modern data science techniques can be used to integrate real-time sensor data streams with robust process-based biogeochemical models for improved predictions of the subsurface biogeochemical response to environmental change. This activity will utilize in situ sensor arrays that we are currently deploying at the Riverton and Slate River sites (c.f., Testing a suite of in-situ sensors for deployment at Riverton and Slate River, below), as well as the RTM simulations underway in Tasks 2 and 3.

Proposed new activity for renewal Science Plan: We intend to build upon newly acquired sensor expertise, modeling expertise, and computer science expertise within Stanford Earth Sciences to investigate novel data science approaches for integrating real-time sensor data into predictive subsurface models. A hybrid data science model will allow for adoption to unexpected system forcings and produce an updated prediction, all in real-time without manual intervention.

Strategic scientific value for CESD: This activity would represent a novel advancement towards the goal of predicting how complex hydrological-biogeochemical systems respond to climate- and human-driven perturbations. The refined modeling approach would also create new paths to rapid process discovery and would provide a new capability for integrating diverse data streams, including aerial imagery.

Surface signatures of subsurface biogeochemical processes. Biogeochemical function varies across watersheds and floodplains in response to varying soil thickness, composition, moisture, permeability, vegetation type, and microclimate. Across the watershed, these parameters may be strongly correlated due to both the underlying depositional processes and the subsequent influence of water and vegetation. In
order to scale the detailed knowledge that can only be developed by focused study at particular sites, the ability to link these parameters through space is critical and has led to the concept of sediment “functional types”. A major question that arises is, “How can we gain an understanding of the diversity and function of molecular-scale biogeochemical processes that are important across this patchwork of domains and by extension define repeating “functional types” ?”

**Challenge:** The current convention for monitoring subsurface biogeochemical activity, i.e., “deep” parameter sampling at a few points in the landscape, is costly, inefficient, introduces unintentional bias and uncertainty, and leaves us blind to subsurface biogeochemical process-function in the rest of the landscape. It also does not allow us to identify repeating functional units across a watershed.

We envision that crucial new scientific discoveries will materialize if we can develop methods of aerially sensed biogeochemical reaction networks using signatures expressed at the landscape surface. Such a capability would transform our ability to scale-up from molecular to landscape domains and to understand more precisely the locations of specific types of reactions.

**Opportunity:** Rapid advances in airborne imaging spectroscopy provide the ability to map the spatial organization of vegetation and associated phenology at floodplain and watershed scales. Many plants are adapted to grow in specific ranges of, e.g., moisture and salt content and redox conditions. The resulting plant communities may also have distinct functional traits and lifecycles, which are known to be reflective of their interactions with belowground fluctuations (e.g., water availability, O₂ levels, etc.) As a result of interdependencies among plant traits and their environment, and the ability to detect both using imagine spectroscopy, the distributions of plant types and phenology can be used to constrain and infer the occurrence of characteristic subsurface biogeochemical conditions.

**Proposed new activity for renewal Science Plan:** We propose to include a subtask in our renewal SFA science plan that would seek to build robust understanding of the relationship between remote sensing techniques that are sensitive to plant communities, traits and phenology, and below-ground hydro-biogeochemical conditions by coupling field investigations with imaging spectroscopy. Specifically, we will: 1) define a candidate set of vegetation and land features that may indicate presence of sediments that experience reducing conditions during some (significant) portion of the year, 2) assess the hydrological contact of groundwater with these sediments, 3) install sensor arrays and porewater/groundwater sampling equipment to monitor the biogeochemical processes and groundwater quality in locations inside and outside of identified areas of interest, in order to 4) validate the diagnostic surface features, and 5) use data science to select and optimize a surface based diagnostic approach for predicting groundwater quality vulnerability in shallow alluvial aquifers. We have expertise in this area in our extended group (including D. Chadwick, Stanford, who is currently analyzing vegetation and soil data to compare with the 2018 NEON imaging spectroscopy data that was collected across the East, Slate and Coal Creek drainages).

**Strategic scientific value for CESD:** This activity would transform our understanding of biogeochemical function at floodplain and watershed scales and allow us to extrapolate our molecular and modeling work to larger portions of the watersheds. It would also dramatically improve our ability to perform spatially explicit modeling predict water quality responses to biogeochemical forcings.

We have begun to discuss these opportunities with CESD program managers. We will continue these discussions as we develop our renewal proposal.

**Testing a suite of in situ O₂, CO₂, and redox potential sensors for deployment at Riverton and Slate River.** Z. Perzan (lead), K. Boye. To support modeling tasks 2.1 and 2.2, as well as improve our understanding of field-scale redox dynamics, we will install an array of water quality sensors across the saturated-unsaturated interface at Riverton and Slate River in 2019. These sensors were procured using
FY17 funds provided by BER for this purpose and will help us to address the low frequency of current weekly manual sampling program, which cannot capture document rapid synoptic redox changes. The two arrays of *in situ* sensors will measure the following subsurface biogeochemical conditions at continuous high frequency: soil moisture, bulk electrical conductivity, DO, CO₂, redox potential, pH, microbial activity, and temperature, as well as porewater concentrations of key redox pairs.

To ensure a successful long-term sensor deployment, we rigorously tested several brands and models of DO, O₂, redox potential, and CO₂ sensors in the lab. After identifying the most accurate and reliable sensor brands, we used modeling and experimental data to rank the value of information provided by each sensor type and plan out two sensor profiles, one at Slate River and one at Riverton (The final sensor arrays will include over 90 individual sensors from 10 different companies (*Figure 8*), including three companies from the SBIR program (Analytical Instrument Systems, Inc.; Burge Environmental, Inc.; and Quantitative BioSciences, Inc.). Powered by solar panels and connected to a datalogger with cellular service, the two arrays will provide our group with real-time information about subsurface biogeochemical conditions.

4.c. **Collaborative research activities with external researchers**

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

**Science Scientific User Facilities:**
- EMSL: 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:**
- Gordon Brown (U. Stanford): Impact sulfidation processes on colloid generation (ST 4)
- Rose Cory (U. Michigan): Reactivity of Fe-organic matter colloids (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)
- Farid Juillot (IRD, France): Inorganic geochemistry of Zn (ST 4)
- Marco Keiluweit (U. Massachusetts) Rhizosphere dynamics (ST 1)
- Stephan Kramer (U. Vienna): Reactivity of mineral transformation generating colloids (ST4)
- Naresh Kumar (U. Vienna): Sulfidation of iron oxides and As fate (ST 3 & 4)
- Laura Meredith (U. Arizona): Microbe-mediated trace gas flux analysis (ST 2)
5. Staffing and budget summary

5.a. Funding allocation by program element (task) and individual researcher. In FY2019, subtasks 2, 3, and 4 comprised about 30%, 45%, and 25% of the total effort, respectively. The largest cost to the project is salaries for postdoctorals and early career scientists. Support for senior personnel is less than 20% of the total budget. Roles and effort for each researcher are reported in Table 2.

Table 2. Specific roles of research personnel in FY 2019. “SU” indicates Stanford University affiliation. “CWC” is Central Wyoming College. RMBL is Rocky Mountain Biological Laboratory.

<table>
<thead>
<tr>
<th>Personnel</th>
<th>Title</th>
<th>Expertise</th>
<th>Role</th>
<th>Subtask</th>
<th>Effort (months)</th>
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<tr>
<td>Tristan Babey</td>
<td>Postdoc</td>
<td>Hydrology</td>
<td>hydrological modeling</td>
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<tr>
<td>John Bargar</td>
<td>Senior scientist</td>
<td>Biogeochemistry, X-ray spectroscopy</td>
<td>Lead PI, Research manager, Scientific lead for subtask 4, Field experiment (Zn) lead, Slate R.</td>
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<td>Lilia Barragan</td>
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<td>Geochemistry</td>
<td>Laboratory support</td>
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<td>Callum Bobb</td>
<td>Student</td>
<td>Biogeochemistry</td>
<td>Field experiments, Reactive transport modeling</td>
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<td>Travel, supplies*</td>
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<td>Kristin Boye</td>
<td>Associate staff scientist</td>
<td>Biogeochemistry, soil science</td>
<td>Scientific lead for subtask 1, field work lead, Riverton, laboratory experiments</td>
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<td>Emily Cardarelli</td>
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<td>Chris Francis</td>
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<td>Jacki Klancher</td>
<td>Associate professor</td>
<td>Water quality assessment</td>
<td>Lead for Riverton field intern team</td>
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<td>Naresh Kumar</td>
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<td>Katherine Maher</td>
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<td>Samuel Pierce</td>
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<td>Zachary Perzan</td>
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<td>Bradley Tolar</td>
<td>Postdoc</td>
<td>Molecular microbiology</td>
<td>Field and laboratory experiments, gene sequencing</td>
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* Salary support for this student is provided by fellowship funding or non-SFA funds (leveraging).

Leveraging. DOE funds are leveraged through collaborations with Stanford graduate students C. Bobb (biogeochemical reactive transport modeling), C. Dewey (biogeochemistry), E. Cardarelli (microbial N cycling), and Z. Perzan (hydrology). We support logistical costs required by these individuals to conduct research. In return, their efforts help to advance SFA program goals. SFA research is also leveraged by DOE-LM support for access to the Riverton field site and for Perzan’s research at the Riverton site.

Scientific user facilities. We are conducting work at EMSL, JGI, and SSRL.

5.b. Funding allocation to external collaborators. A subcontract to Dr. Jackie Klancher (Central Wyoming College, CWC) supports sampling activities at the Riverton site performed by undergraduates.
A subcontract to the Rocky Mountain Biological Laboratory, RMBL) supports an intern who is performing field work for our program.

5.c. Personnel actions and procedures. T. Babey was recruited to join the SLAC SFA team as a postdoc to lead our unsaturated zone reactive transport modeling activity.

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). While not capital equipment, these items are expensive and difficult to accommodate in our budget; As described in section 4.b. (Surface signatures of subsurface biogeochemical processes), we would like to begin imaging surface features to gain additional information on subsurface processes and to enable intelligent site selection for future installations of subsurface sampling and measurement devices. We would like to purchase an unmanned aerial vehicle (UAV) equipped with a camera and filters for multispectral imaging. The cost for such a system would be about $20,000.

Tangential flow filtration (TFF) is a rapid and efficient method for purification and concentration of colloids from small volumes of porewater obtained from the field and laboratory. Having concentrated samples of otherwise highly dilute colloids would greatly facilitate molecular-scale characterization by XAS, FT ICR-MS, FI-IR spectroscopy, and other methods in our core program. Field flow fractionation (FFF) is highly complementary to TFF because it can size separate and characterize colloids from 1 nm to 1 μm. The combination of FFF and ICP-MS provides size, detection, and compositional analysis at the parts per billion (ppb) levels. We would like to purchase a TFF system for about $10,000 and an FFF system for about $30,000 to improve our colloid and organic matter research programs.

References Cited. Citations 1-17 are listed in Appendix A.
Appendix A. List of publications and presentations

6.a. Comprehensive list of publications wholly or partly supported by this program, June 30, 2018 – June 30, 2019.

Manuscripts that are published, in press, or have been submitted


Manuscripts in preparation during FY 2019 for submission in FY 2020


Manuscripts from collaborations with external groups


6b. Presentations at National and International Scientific Meetings wholly or partly supported by this program June 30, 2018 – June 30, 2019.

Oral presentations at national and international science meetings. Numerical order continued from References Cited section, above..


