FWP 54737

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Pacific Northwest National Laboratory SFA Annual Report

Hydro-Biogeochemical Process Dynamics in the Groundwater-Surface Water Interaction Zone

June 2016

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

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PNNL SBR Scientific Focus Area Annual Report FY2016

Hydro-Biogeochemical Process Dynamics in the Groundwater-Surface Water Interaction Zone

2016 Annual Report

June 30, 2016

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I. PROGRAM OVERVIEW

The transient movement of surface water to and through aquifer systems results in significant modifications to its thermal, chemical, and microbiological properties depending upon the nature of the subsurface environment, contact time, and other factors. As groundwater re-emerges at the Earth's surface, it mixes with geochemically and microbiologically distinct surface waters in a critical ecotone we define as the subsurface interaction zone (SIZ). The subsurface interaction zone is a domain of temporally variable extent where groundwaters and surface waters mix in response to water cycle dynamics. It includes the hyporheic zone and domains of the associated aquifer and groundwater system that experience water table elevation changes and river water intrusion as a consequence of river stage variations. The subsurface interaction zone is a key compartment of a river corridor, being mainly responsible for the resilience of riverine systems in the face of environmental change.

In the semi-arid western U.S., aquifers are typically oligotrophic (carbon-poor) but enriched in nitrogen (N), and conversely surface waters are nitrogen-limited but contain significant organic carbon (C) from primary production. Thus the subsurface interaction zone is a domain of confluence of key nutrients, and a potential hotspot of increased biogeochemical activity that tranforms inputs of N and processes large amounts of organic C. Rivers also serve as the primary environmental receptor for groundwater contaminants, with the subsurface interaction zone serving as the last line of defense against the discharge of mobile nutrients and contaminants to surface water. Consequently, a scientific understanding of the subsurface interaction zone is fundamental to effective predictions of 1) the dynamics and resilience of natural and perturbed watersheds, 2) C/N feedbacks to climate in coupled groundwater-surface water systems, and 3) water quality including its thermal regime and the fate and transport of anthropogenic contaminants.

Because of the importance of the subsurface interaction zone to watershed function, and the critical role of watersheds to water supply and biogeochemical cycles influencing climate climate, Pacific Northwest National Laboratory's (PNNL) Subsurface Biogeochemical Research (SBR) Scientific Focus Area (SFA) is addressing a grand research challenge focused on this poorly understood terrestrial interface. *PNNL's SFA will develop a predictive understanding of the groundwater-surface water interaction zone and its linkages with the water cycle that incorporates hydrologic impacts on biogeochemical and ecological processes into a multi-scale modeling framework that can be used to understand and predict system responses and feedbacks to environmental changes.* This challenge will meet an important BER/CESD goal to advance understanding of the "critical role that biogeochemical processes play in controlling the cycling and mobility of materials in the Earth's subsurface and across key interfaces in the environment".

II. KEY SCIENTIFIC QUESTIONS UNDER INVESTIGATION

We have selected a subsurface interaction zone system that is ideally suited to address our grand challenge in terms of multiscale character, mission impact, and national significance, while also building on past investments and scientific progress. Specifically, our research is being conducted on an iconic river corridor system in Washington state (the Columbia River), beginning with local, kilometer-scale, river bank studies at the Hanford 300 Area where uranium contamination exists, and expanding to the Hanford Reach, an 80-km stretch of the Columbia River that defines the north and east boundaries of the U.S. Department of Energy (DOE) Hanford Site. The Hanford Reach displays an extensive and dynamic subsurface interaction zone, termed a hyporheic corridor, that is representative of other large, gravel-dominated alluvial systems in North America.

Eight Hanford contaminant plumes currently discharge through the interaction zone to the west side of the Hanford Reach, while irrigation waters and groundwaters with agricultural residues discharge from the east. Active hyporheic zone biogeochemical cycling of carbon and nitrogen occurs on both sides of the Reach (presumed) leading to biogenic gas flux from the riparian zone and river. In the longer term, our work will be broadened to the entire Columbia River Basin (CRB), and extended to other impactful field sites in the Basin to validate our findings and models at the watershed scale. The CRB is a highly managed and regulated watershed that is archetypical of the land-water-energy nexus as it hosts the nation's largest hydropower and irrigation systems, and faces complex water availability, ecosystem function, water quality, and fisheries management issues. It is a system of concern to multiple state and federal agencies. Sizable impacts have resulted to the ecosystem from energy and agricultural activities, and the Basin and its extensive managed infrastructure is highly vulnerable to the effects of climate change.

We are addressing four, overarching science questions related to how the subsurface interaction zone regulates impacts to, and controls the resilience and adaptability of the linked groundwater-surface water hydroecosytem within a managed, perturbed watershed.

1) What are the dynamics and spatial extent of the subsurface interaction zone, what is the volume and residence time of surface water – groundwater exchange, and how will these change in the future with non-stationary climate? How do hydrophysical and biogeochemical processes in the subsurface interaction zone influence water quality and ecosystem function at the local and reach scales?

2) How do subsurface interaction zone processes control and modulate chemical fluxes (C and N, biogenic gases, and contaminants) between groundwater, surface water, and the atmosphere? What controls the nature and distribution of biogeochemical processes at different sites and at different scales, and what constitutes an acceptable system-scale model?

3) What key microbial ecologic and functional parameters are needed to describe biogeochemical processes and transformations in reactive transport models for robust prediction of the temporally and spatially dynamic, multiscale behavior of the subsurface interaction zone?

4) What hierarchies exist for subsurface interaction zone processes in moving from the bank, to the reach, and to the watershed scale? How can knowledge of process hierarchy and physicochemical properties distributions captured by a facies-based classification scheme be used to establish an integrated multiscale framework to robustly include the subsurface interaction zone in Earth System Models and the assessment of impacts, adaptations, and vulnerabilities of the Columbia River Basin?

III. NATIONAL LABORATORY PROGRAM STRUCTURE

The PNNL SBR-SFA is overseen by a Laboratory Research Manager (Charlette Geffen), a Principal Investigator (John Zachara), and two Co-P.I.s (Jim Fredrickson and Tim Scheibe) (Figure 1). These individuals constitute the SFA management team. The SFA has five Tasks and five Task Leads (Figure 1). Task Leads manage the development of yearly research plans, and track and report progress toward milestones described in the Science Plan. The P.I., the Co-P.I.s, and the Task leads constitute the SFA scientific leadership team that meets monthly. The contributing staff, including funded collaborators, are key disciplinary experts that work together in cohesive, highly interactive teams around experimental or modeling campaigns to accomplish Task objectives and resolve hypotheses. Additional details on our management structure and philosophy are provided in our FY 15 Science Plan.

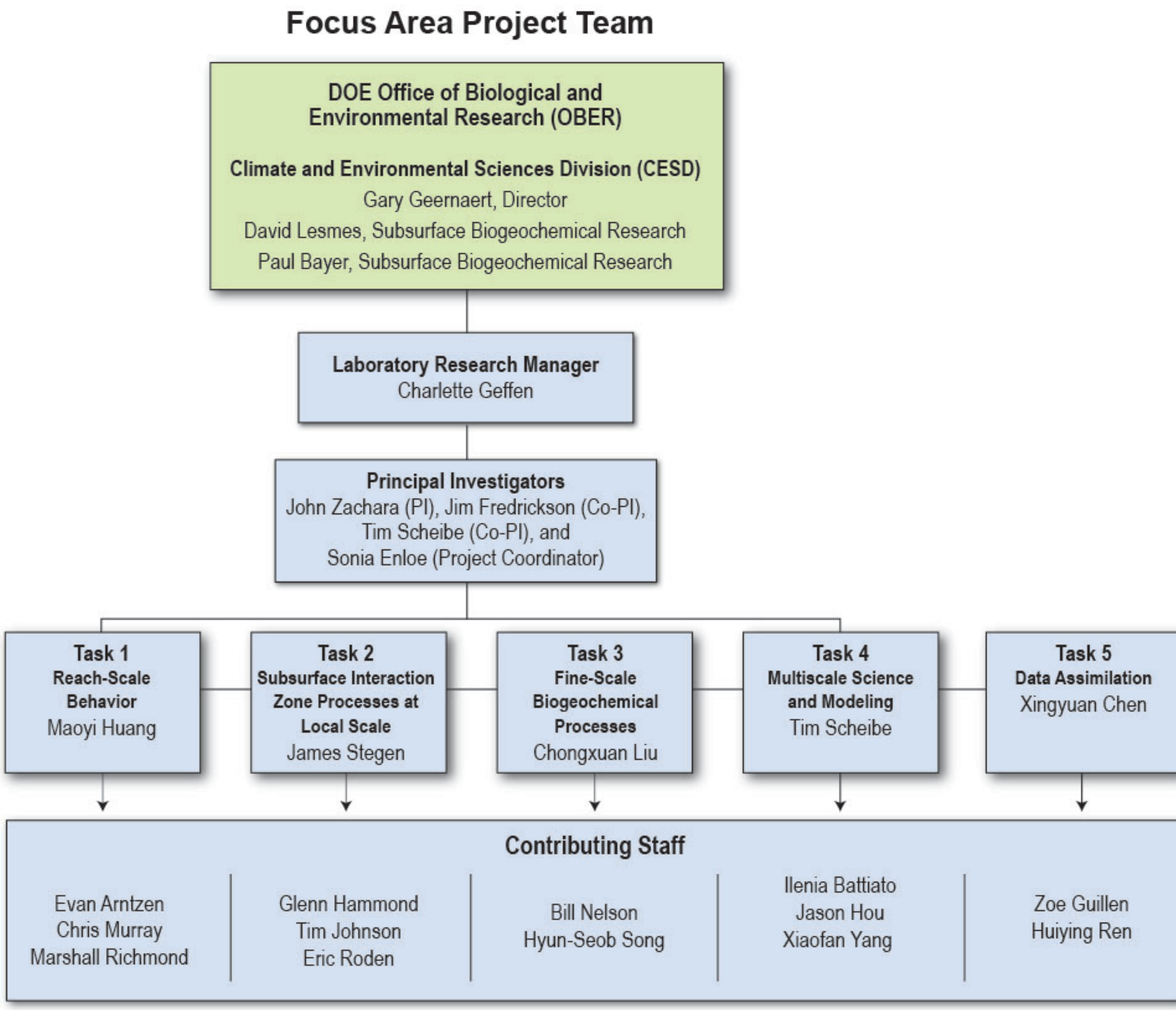

Figure 1. FY 16 PNNL SBR-SFA Project Team.

IV. PERFORMANCE MILESTONES AND METRICS

Review of Scientific Progress Toward Program Objectives and Milestones

<u>Task 1: Reach Scale Behavior</u>

Overall Objective

The objectives of this task are to: 1) develop a facies-based classification scheme of subsurface interaction zone environments along a river reach to enable simulations and predictions of contaminant, C, and N fluxes from different system compartments; and 2) improve reach-scale understanding of the spatial and temporal dynamics of biogeochemical cycling in the subsurface interaction zone, their interactions with the water cycle, and feedbacks to climate through observational studies, data synthesis, and integration of results into reach-scale models that include the land surface, groundwater, the subsurface interaction zone, and river.

This task contributes to the SFA by assessing the effects of daily, seasonal, and yearly variations in the hydrologic cycle and climate on groundwater-surface water interactions, contaminant mobilization and transport, and C and N aqueous concentrations and gaseous fluxes from the subsurface interaction zone at the reach scale. Feedbacks to climate will be assessed by incorporating subsurface interaction zone process understanding, biogeochemical and ecologic models, and hydrogeologic structures into the DOE ESM under development in the Accelerated Climate Modeling for Energy (ACME) project (denoted ACME ESM).

FY16 Research Targets

The primary goals and research scope for FY 16 are to: 1) perform integrated land-water-atmosphere simulations to better understand the effects of spatio-temporal variability in hydrologic regimen on groundwater-surface water and land-atmosphere exchanges; 2) conduct reach-scale field campaigns to quantify gas and liquid fluxes from the subsurface interaction zone (including the use of eddy covariance towers and field surveys in coordination with Task 2 to quantify land-atmosphere and water-atmosphere exchanges); 3) simulate CRB hydro-climatic conditions to provide boundary conditions and future hydrologic scenarios for reach-scale terrestrial and river models; and 4) assemble the initial reach-scale facies model in collaboration with Task 4.

Progress Brief for FY15-16

FY16 Science Plan Milestone: Incorporate subsurface interaction zone processes into terrestrial and riverine models. Calibrate and validate the models against observations at the local scale. Complete development of the initial reach-scale facies model.

Subsurface interaction zone processes were incorporated into the coupled terrestrial and riverine model CLM-PFLOTRAN in FY15. In FY16 the model was extended to longer time periods and larger spatial domains to prepare for reach-scale applications. Vegetation and meteorologic parameters for CLM were collected from site surveys and local meteorological stations. The PFLOTRAN vertical domain was extended from the soil surface to the Hanford-Ringold contact, using measured subsurface properties from the site. The lateral boundary conditions for CLM and PFLOTRAN were provided by groundwater monitoring wells and observed/simulated river stages. Calculations at multiple resolutions (i.e., 2m, 10m, and 20m) for a 400m x 400m domain along the Columbia River shoreline were configured and performed over a five-year period (i.e., 2011-2015) spanning high and low river flow conditions. Modeling goals were to: 1) quantify the impact of groundwater-river interactions on surface and subsurface hydrologic states and fluxes under different hydrodynamic conditions; and 2) assess the impact of spatial resolution on simulated variables of interest to establish a basis for upscaling. A configuration of the model over a 7-km reach using an initial reach-scale facies model was also established. Numerical experiments were performed to determine the best approach for coupling surface and subsurface domains.

A 3-D computational fluid dynamics (CFD) model that solves the Navier-Stokes equations was also configured for the 7 km reach domain to simulate river and subsurface flows simultaneously. A series of CFD simulations were performed to better understand hyporheic flow patterns and exchange rates under different river stage and velocity conditions, as well as to isolate the roles of geomorphological features and channel structures, including islands and bars, on calculated hyporheic flow patterns and exchanges.

A number of different field observations were performed to quantify the role of the subsurface interaction zone on groundwater-surface water and land-atmosphere exchanges for both model development and validation. Field campaigns were conducted using: 1) flux towers along the Hanford Reach corridor to monitor land, wetland, and surface water energy and CO_2 fluxes; 2) temperature sensor arrays deployed along the riverbed to monitor heat fluxes between the river and hyporheic zone (representative of water exchanges); and 3) flow meters and acoustic doppler current profiling to establish river velocity distributions at seven channel cross sections.

An existing configuration of the Modular Aquatic Simulation System in One Dimension (MASS1) was applied to the Hanford Reach to provide boundary conditions for integrated surface and subsurface simulations. MASS1 is a river routing model that uses a LiDAR-based bathymetric model of the Hanford Reach channel structure, hourly inflow volumes to the Priest Rapids dam pool, hourly meteorologic data from the Hanford Meteorological Station, and surface elevations at the McNary Dam as input parameters and forcing. In addition, a large-scale hydrologic model, featuring the coupling between the Variable Infiltration Capacity (VIC) model, the river routing model MOSART, and the Water Management (WM) model, was configured and calibrated to provide large-scale hydro-climatic boundary conditions for the reach- and local-scale models. Simulations of VIC-MOSART-WM were performed for 1975-2100, and included a historical period and a future period with two climate scenarios.

An initial facies model has been configured for reach-scale model simulations. Facies are defined for: 1) the subsurface aquifer adjacent to and beneath the Columbia River (subsurface facies); and 2) the riverbed alluvial sediment (riverine facies) that includes the hyporheic zone. Hydraulic properties of subsurface facies vary with facies type based on the statistics of borehole measurements and pumping/slug test experiments performed at the IFRC well-field. Riverine facies were spatially mapped along a 7-km river corridor section using river bathymetric and hydrodynamic attributes as primary diagnostic variables. Hydrologic and biogeochemical properties were assigned to facies based on measurements performed on sediment cores.

Plans for FY17

Future research will address three primary activities. 1) Finalize a modeling approach for reach-scale integrated surface and subsurface simulations by assessing the impacts of model resolution, coupling strategy, and subsurface/riverine facies configurations. Perform reach scale simulations using the final conceptual model. 2) Design and execute field campaigns and integrate data into the reach-scale model to quantify hyporheic flow patterns and exchange rates in different geomorphic and hydraulic settings within the Hanford Reach and their controlling factors in collaboration with Task 2. 3) Enhance instrumentation at the flux towers and associated monitoring locations to support ecohydrological studies.

Task 2: Subsurface Interaction Zone Processes at Local Scale

Overall Objective

The objectives of this task are to: 1) develop a comprehensive understanding of the hydrologic, geochemical, and microbial ecologic processes affecting biogeochemical dynamics at local scales (100 to 500 m) in the subsurface interaction zone through multi-disciplinary field experiments linked with system-scale geophysical monitoring; and 2) iteratively encode new understanding in a coupled-process, local-scale model that predicts, with quantified uncertainty, the effects of the hydrologic cycle on the distribution of microbial functional guilds and the biogeochemical processes they catalyze across the subsurface interaction zone.

This task contributes to the SFA grand research challenge by conducting multi-investigator field and modeling studies associated with the yearly hydrologic cycle to assess the biogeochemical functioning of the subsurface interaction zone at the local scale across highly variable hydrodynamic conditions. New understanding, linked to a detailed local physical model of the Columbia River subsurface interaction zone, will drive the development of predictive models of contaminant and C/N-cycling dynamics generalizable to other local-scale sections of the hyporheic corridor for reach-scale modeling and assessment.

FY16 Research Targets

The primary goals and research scope for FY 16 are to: 1) characterize the structure of physical properties, biogeochemical processes, and microbial community composition and function existing across the groundwater-surface water interaction zone; 2) develop a predictive ecological model for microbial community composition and function influenced by dynamic hydrologic conditions; 3) quantify spatiotemporal dynamics in aqueous biogeochemistry and organic carbon source terms through natural field experiments; and 4) calibrate and validate a local-scale hydro-biogeochemical model, based on reaction networks from Task 3 and through assimilation of geophysical measurements and interaction zone monitoring data.

Progress Brief for FY15-16

FY16 Science Plan Milestone: Calibrate and validate a local-scale hydro-biogeochemical model through assimilation of 4D geophysical and direct monitoring data, and develop a predictive ecological model with validation at the local scale.

Aqueous and colonization-substrate samples collected from the river, the near-shore hyporheic zone, and across the broader aquifer revealed that substrate-attached microbial communities respond to hydrological shifts on a seasonal time scale, while unattached microbial communities respond to sub-hourly shifts in groundwater-surface water mixing. Results also indicated that a shift from river water to groundwater conditions in the hyporheic zone shifts microbial function from heterotrophic metabolisms that oxidize organic carbon and generate CO_2, to autotrophic nitrifying metabolisms that fix CO_2 and generate nitrate. Further analyses connected ecological community assembly processes to ecosystem function and enabled collation of results into a novel conceptual model. In this conceptual model, temporally-stable and dynamic ecological selective forces combine to govern ecosystem function, measured in our field site as aerobic metabolism normalized to microbial biomass. Additional field efforts coupled with high resolution characterization of dissolved organic matter, in collaboration with EMSL, also revealed that shifts in carbon cycling processes are associated with deterministic shifts in microbial community composition, and that molecular transformations of N-containing organic compounds are overrepresented in the hyporheic zone and are effectively absent in river water.

In collaboration with Task 4, grain size distributions from shoreline freeze cores were coupled with assays of microbial activity and community composition to evaluate the potential for physical controls over biogeochemical function. These analyses revealed a remarkably high and spatially-consistent dominance of nitrifying microorganisms that were similar to those observed in work summarized above. Freeze cores were collected at a time of groundwater discharge, which is consistent with a shift toward autotrophy during groundwater conditions. The analyses further characterized spatial variation in local sedimentary facies and found that sediment-associated organic carbon and nitrifying microbial taxa increased with the fractional contribution of larger grain sizes. This suggests that a physically-based facies approach can be used to predict key microbial taxa and important biogeochemical parameters. Analyses of additional freeze cores further revealed significant differences in biogeochemical activity across larger-scale ‘riverine facies’ (delineated by Task 4) and between sediments with different apparent organic carbon sources and free energy. Free energy estimates are being coordinated with Task 3 efforts with the aim of providing thermodynamic and kinetic measurements relevant to biogeochemical reaction networks. The free energy estimates will be coupled with shotgun metagenomic and metaproteomic measurements to evaluate coordinated shifts in microbial metabolism and carbon chemistry. The resulting samples are being analyzed through collaborations with EMSL and the Earth Microbiome Project.

In collaboration with Task 1 a boat-towed thermistor array was developed and deployed at the field scale with the purpose of mapping groundwater discharge zones using temperature as a tracer. This effort revealed significant spatial variation in the presence/absence of groundwater discharge zones. The resulting patterns have been used to design field campaigns for both Task 1 and Task 2. For example, vertically distributed temperature sensors were deployed at locations that vary in the presence of groundwater discharge. The resulting data are being used by Task 1 to estimate vertical hydrologic fluxes and by Task 2 to inform local-scale hydro-biogeochemical simulation modeling. The towed thermistor data were also used in conjunction with Task 4 characterization of both subsurface and riverine facies. The thermistor array has been made available to Task 1 for reach-scale investigations.

A conceptual model of alluvium layer shape was developed from freeze coring and slug testing. This conceptual model was used to construct a 2D model perpendicular to river flow using PFLOTRAN. The resulting model was passed to Task 4 to support multi-scale modeling efforts. In coordination with Task 5, an ensemble-based data assimilation method was developed for estimating the alluvium layer shape based on field-collected pressure data. Different configurations of piezometers were compared *in silico* to provide guidance on the spatial layout of a field-deployed piezometer network, which was subsequently installed and instrumented. A field-scale hydro-biogeochemical model was also formulated within PFLOTRAN based on the 2D flow model. Prior to pressure data becoming available, *in situ* temperature data from hyporheic zone piezometers were used to track groundwater-surface water mixing. These data were assimilated within PFLOTRAN to estimate alluvium and aquifer permeabilities. The calibrated 2D model was able to capture flow dynamics observed in the hyporheic zone. Within the calibrated model, dissolved oxygen data from river, hyporheic zone, and aquifer compartments were used to estimate aerobic respiration rate parameters. However, numerous challenges were revealed in attempting to model this complex and dynamic system. For example, a temperature inversion was observed—with cool sediments between warm end members—that departed from the initial conceptual model. Additional monitoring of hyporheic zone dissolved ions is therefore required to track mixing dynamics. Monitoring of additional redox active solutes as markers of biogeochemical dynamics was also affirmed as a priority for ongoing field activities. In addition, the 2D PFLOTRAN model was utilized within the PFLOTRAN-E4D framework to numerically investigate mixing dynamics using a high-resolution riverbed 4D ERT monitoring array. This study validated the capability to identify spatial and temporal mixing dynamics, and the stage conditions under which ERT data must be collected in order to provide optimal resolution of shifts in pore water composition.

Several other important activities have been initiated. In support of Task 4 modeling needs, a large and intact freeze core was collected and is slated for multi-scale imaging of pore structure. The resulting data will be used to inform Task 4 multi-scale flow models. The data will also be used to design spatially-explicit sampling within the core aimed at quantifying microbial activity—across a range of hydrologic environments—toward key redox processes such as nitrification and denitrification. In support of Task 3 enzyme and mRNA based modeling efforts, sediment samples are being collected across seasons and across riverine facies with the purpose of quantifying specific enzyme and mRNA concentrations *in-situ*; these data are needed to constrain the application of Task 3 models to the field. Significant efforts have also been made to generate spatiotemporal datasets needed to calibrate and evaluate local-scale hydro-biogeochemical modeling efforts. These include 4D geophysical imaging datasets that will inform hydrological parameters that control mixing dynamics. Additional instrumentation is slated for installation this FY; the spatial layout and measured parameters are being closely coordinated between field researchers and modelers. The instrumentation design is also being informed by near-shore 4D geophysical imaging that has provided much higher spatial resolution of preferential flow paths relative to previous efforts deployed further inland. Lastly, to provide a biogeochemical component to Task 1 modeling efforts, empirical patterns of dissolved organic carbon dynamics are being coupled with Task 1 hydrologic predictions in order to estimate the quantity of organic carbon processed in the hyporheic zone as consequence of river water intrusion.

Plans for FY17

Key targets for future local scale research include the following four activities. 1) Expand the local-scale biogeochemical transport model to include heat transport, temperature dependent reactions, and an updated biogeochemical reaction network informed by both lab experiments and field observations. 2) Estimate *in situ* biogeochemical rates represented in the updated reaction network to constrain rate parameters, and empirically link rate measurements to microbial community properties to be used as easily measured proxies of biogeochemical rates. 3) Generate multi-season datasets on hydrologic and biogeochemical conditions in the hyporheic zone and assimilate those long-term datasets within the local-scale modeling platform to provide a predictive modeling capability. 4) Link hydrologic setting and organic carbon inputs to the spatial structure of redox processes, both within and across riverine facies.

Task 3: Fine-Scale Biogeochemical Processes

Overall Objective

The objectives of this task are to: 1) develop a mechanistic understanding of key biogeochemical reactions, kinetic pathways, and transport processes controlling C, N, and contaminant concentrations and fluxes in the subsurface interaction zone; 2) establish process-based reactive transport models that incorporate fundamental biogeochemical mechanisms and microbial community metabolic dynamics; and 3) evaluate approaches to integrate subgrid heterogeneity in microbiological, geochemical, and hydrophysical properties and different facies types into process-based models for predictions of system behavior at the local scale.

This task contributes to the overall SFA grand research challenge by quantifying mechanistic aspects of coupled hydrologic and biogeochemical processes at the fine scale (0.001 to 0.5 m) that control the fate and transport of contaminants (Cr, Tc, and nitrate) and the production of gaseous species (CO_2, N_2O, and CH_4) in interaction zone sediments. Biogeochemical reaction networks and process-based transport models are being developed for field and multiscale integration and applications.

FY16 Research Targets

The primary goals and research scope for FY 16 are to: 1) characterize subsurface interaction zone sediments to establish reaction networks and kinetics governing N-cycling and chromium transformation; 2) optimize a targeted proteomics approach to quantify the dynamics of functional enzymes and their linkage with biogeochemical reaction kinetics in the sediments using microbial denitrification as an example; and 3) develop functional enzyme-based models for simultaneously describing microbial community functions and biogeochemical reactions.

Milestone and Progress Brief for FY15-16

FY 16 Science Plan Milestone: Establish reaction networks and dominant biogeochemical pathways for the in-situ microbial community, and use these to describe the rates of contaminant redox transformation, organic C degradation, and flux of gaseous species. Develop and evaluate a genome-informed biogeochemical model.

Sediments from Columbia River 300A hyporheic zone were collected in collaboration with Task 2, and have been characterized to determine important biogeochemical processes governing N-cycling under dynamic flow conditions, and to quantify the coupled redox transformations of Cr, Fe, O_2, and organic carbon that control Cr reduction and reactive transport in the hyporheic zone. The results indicated that denitrification, dissimilatory nitrate reduction to ammonium (DNRA), and aerobic and anaerobic ammonium oxidation collectively controlled N-cycling in hyporheic zone sediments. A reaction network was established that represents N-cycling biogeochemical processes and their coupling. The research also revealed that functional gene abundances, and thus microbial community function potentials, evolved quickly along flow direction in response to changes in fluid chemical composition, oxygen concentration, and residence time. Dominant biogeochemical processes thus showed dynamic zonation that affected the concentrations and spatiotemporal distributions of nitrogen species, organic carbon composition and oxidation state, and sediment redox conditions. Associated batch experimentation found that the rate of ammonium oxidation was affected by ion exchange, which controlled the partitioning of ammonium between solid and aqueous phases, and thus the bioavailable concentration.

A functional enzyme-based model framework was established to link the biogeochemical reaction network with enzyme synthesis dynamics. The model exploits a newly developed SFA technology based upon a BER Early Career Award to Wei-Iun Qian for quantification of enzyme abundance and dynamics in sediments with complex matrix and low biomass. Model-simulated enzyme dynamics, a key variable in the enzyme-based model framework, can thus be validated using the measured values. The model has been successfully evaluated for denitrification. It will be further challenged under more complex conditions including the presence of O_2 that can inhibit nitrate reductase growth and/or activities, and/or other N-transformation pathways such as nitrification. The experimental data for these more complex conditions are currently being collected and will be used in testing the functional enzyme-based model in FY16-17.

Experimental and modeling studies were also performed to investigate chromium [Cr(VI)] reduction (immobilization) and reactive transport in sediments under both laboratory and field-scale hydrological conditions. Hexavalent chromium is a primary hyporheic zone contaminant at the Hanford Site that is toxic to spawning salmon. Hexavalent chromium immobilization within hyporheic zone sediment was regulated by the complex coupling of Cr, Fe, O_2, and organic carbon (OC) biogeochemical interactions. Microbial regeneration of Fe(II), abiotic Fe(II) oxidation by oxygen, organic carbon bioavailability, oxygen supply rate, and fluid residence time all influenced the rate of Cr(VI) reduction. A reaction network and kinetic model was established to describe the coupled Cr, Fe, O_2 and OC transformation. Simulations using the model under field-relevant hydrological conditions indicated that Columbia River hyporheic zone sediments have a rechargeable reduction capacity for reducing and thus immobilizing Cr(VI). Sensitivity analysis revealed that residence time and organic carbon bioavailability are the two most important factors controlling the transport and immobilization of Cr in the hyporheic zone and the extent of its discharge to the Columbia River.

Plans for FY17

Fine-scale biogeochemical process research will focus on three primary activities over the next fiscal year. 1) Expand the targeted protein measurement technique and functional enzyme-based kinetic model to include ammonium oxidation enzymes, reactions, and kinetics as they occur in hyporheic zone sediment. 2) Develop approaches to integrate organic carbon composition, speciation, and free energy into biogeochemical reaction networks for C, N, and Cr using FTICR analyses of hyporheic zone organic carbon (dissolved and sediment bound) and composition-based free energy analyses. 3) Develop a reactive transport model that integrates the enzyme-based metabolic model for biogeochemical reactions with fine-scale facies heterogeneity (subgrid effects) for describing the reactive transport of C, N, and Cr [collaborative with Tasks 2, 4, and 5].

Task 4: Multiscale Science and Modeling

Overall Objective

The objectives of this task are to: 1) analyze linkages among fine-scale process models (Task 3), local field-scale models (Task 2), and reach-scale models (Task 1); 2) determine the set of information required by each at-scale model and the conditions under which various approaches to multiscale model coupling are applicable; 3) implement and test the identified approaches and data linkages as specific coupling algorithms to develop a flexible multiscale computational capability integrating Task 1-3 models; and 4) apply the integrated multiscale modeling capability to address SFA science questions and knowledge gaps related to interaction zone function and impacts at the reach scale.

FY16 Research Targets

The primary goals and research scope for FY16 are to: 1) refine hierarchical facies definitions at fine, local and reach scales; 2) define facies mapping techniques at the local and reach scales based on surrogate measures; 3) evaluate facies-based applicability regimes for upscaling fine-scale processes; and 4) integrate 3D riverbed and aquifer facies distributions and denitrification reaction networks from Task 3 into a multiscale simulation framework and test against field measurements.

Progress Brief for FY15-16

FY16 Science Plan Milestone: Implement two-scale model linkage (fine and local scales) and perform a suite of multiscale simulations to define impacts of subsurface interaction zone exchange on U release to the Columbia River at the 300 Area. Define facies-based applicability regimes for upscaling local-scale U reactive transport to the reach scale and identify multiscale modeling methods for linking local- and reach-scale models of water and solute mass exchange (with Tasks 1 and 2).

Facies definitions and mapping: Facies are elements of a classification scheme that conceptually simplify the complexity of natural geologic heterogeneity and provide a framework for assignment of parameters in numerical models. Facies are traditionally defined based on physical factors such as grain size distribution, mineralogy, and sedimentary structures, but the facies concept has been extended to include other material attributes such as geophysical response, biogeochemical activity, and hydraulic properties. In FY16 we have developed a facies classification scheme for the two primary geologic components of the subsurface interaction zone: 1) the groundwater aquifer adjacent to and beneath the Columbia River (*subsurface facies*); and 2) alluvial sediment comprising the hyporheic zone (*riverine facies*). Subsurface facies distributions control the spatial extent and timing of inland river water intrusion and associated biogeochemical impacts. Subsurface facies were defined and mapped based on extensive historical studies at the Hanford Site, and spatial distributions and hydraulic properties were assigned based on available well log and hydraulic testing data. Subsurface facies maps are being used for both local- (Tasks 2/4) and reach-scale (Task 1) modeling of hyporheic exchange.

Riverine facies control hyporheic exchange within the riverbed where biogeochemical activity is enhanced. Riverine facies were initially defined from grain-size measurements, after which co-located sediments were collected for chemical and biological analyses. Multivariate analysis of the facies and biogeochemical data facilitated the definition of *biogeochemical facies* in which biogeochemical attributes were related to sediment textural properties. An observed high correspondence between sediment texture (especially the percent of sand-sized sediment) and multiple biogeochemical attributes demonstrated that biogeochemical property distributions could be inferred from maps of sediment texture. We propose a conceptual model in which areas of greater water flux (sand rather than silt and mud) have higher sustained oxygen and organic carbon levels due to increased exposure to river water, and therefore increased heterotrophic activity and microbial biomass. Utilizing this information in numerical models requires mapping the spatial distribution of textural facies based on surrogate data for which a high degree of spatial coverage is available. For the riverine facies, texture is controlled by river bathymetric and hydrodynamic attributes such as bed shear stress. The river model MASS2 was used to simulate the spatial distribution of hydrodynamic shear stress in a 7-km reach of the Columbia River adjacent to the 300 Area. Riverine facies were defined by dividing the distribution of simulated shear stress into four quartiles. The facies so defined were shown to correlate well to alluvium texture, and the resulting riverine facies maps are being used in local- and reach-scale numerical models.

Multiscale modeling framework development: A key feature of our multiscale approach is the combination of upscaling methods with more complex hybrid multiscale methods. Work was completed on a theoretical and numerical analysis of a novel two-stage upscaling method, applicable to media in which two dominant length scales are evident, representative of the riverine facies in which large gravel clasts are infilled by a finer-grained matrix. Subsequent application of the method to observed pore geometries from 300-area sediment cores indicated the need to address porosity that is below the resolution of routine x-ray tomography (~50 microns), so a downscaling method to simulate the sub-resolution porosity distribution was developed and successfully tested against laboratory tracer observations. Ongoing work is incorporating Cr reactions into this framework to evaluate its applicability for defining facies-based parameterizations for use in local-scale models.

We previously developed and tested a hybrid multiscale modeling framework that facilitates the coupling of two or more simulation codes operating at distinct scales. The framework has been successfully extended to simulate groundwater and river water exchange at the 300 Area local field study site. The multiscale framework utilizes two distinct scales of PFLOTRAN simulators, one to represent the thin alluvium layer with high resolution and a second to represent the larger subsurface aquifer domain with coarse resolution. A simulation using homogeneous property distributions was compared to the Task 2 single-scale model to validate the method. The model was then used to evaluate the impact of heterogeneity within the alluvium layer (which cannot be explicitly addressed in the single-scale model). We are currently incorporating a more complex biogeochemical model of denitrification (from Task 3) into the multiscale framework. We have shifted our focus from the milestone target of U transport, to processes more relevant to alluvium biogeochemistry (Cr transport and denitrification) as new models have become available from Task 3 studies. Alternatives to the hybrid multiscale method, including the multiscale finite volume and multi-level Monte Carlo methods, are being evaluated for accuracy, computational efficiency, and ability to quantify uncertainty.

Plans for FY17

Four key targets for multiscale science and modeling will be pursued. 1) Perform pore-scale simulations based on Task 3 reaction networks and parameters, and apply upscaling methods to define flow and reactive transport properties for riverine facies for use in local-scale simulations. 2) Collaborate with Tasks 1 and 2 to design field experiments for multiscale model validation. 3) Expand facies models to the full Hanford Reach and define hierarchical relationships between reach- and local-scale facies. 4) Implement a multiscale modeling approach for the Hanford Reach with Task 1, incorporating key processes and properties such as volumes of interaction zone water exchange and their residence times as influenced by geomorphic features and channel structures.

Task 5: Data Assimilation and Management

Overall Objective

The objectives of this task are to: 1) establish and maintain a central repository for processing, quality assurance and control, storage, and dissemination of project experimental and modeling datasets; and 2) improve the predictability of SFA models through iterations between model conceptualization and experimental/field data collection. This activity is key to the development of a systematic model and predictive capability for the groundwater-surface water interaction zone across multiple scales as needed to resolve our research grand challenge.

FY16 Research Targets

Our goals and research scope for FY 16 are to: 1) develop a sensitivity analysis method that is capable of identifying the most important uncertainty sources for complex hydro-biogeochemical models, and that considers their intrinsic hierarchical dependence and spatial heterogeneity; 2) develop efficient facies-based data assimilation methods to facilitate integration of indirect field observations for facies-based parameter estimation; and 3) build a repository for data preservation, quality assurance and uncertainty quantification, integrated analysis and multi-process interpretation, and dissemination of project results to the scientific community.

Progress Brief for FY15-16

FY16 Science Plan Milestone: New Task since submission of FY 15 Science Plan.

We developed a new variance-based sensitivity analysis method based on the hierarchical uncertainty quantification framework to identify important uncertainty sources in biogeochemical transport models of complex environmental systems. This new sensitivity analysis approach was applied and tested against a robust dataset from a dynamic tracer experiment performed within the subsurface interaction zone of the Hanford 300 Area. Among the three main uncertainty sources of the numerical model: dynamic flow boundary conditions, contact elevations of transmissive and aquitard sediments, and permeability field; our analyses identified boundary conditions and permeability field to be the most important uncertainty source for simulated hydraulic head and tracer concentrations. Our spatial and temporal analysis of sensitivity revealed that a more simple assessment based on fixed location or time point cannot capture the overall sensitivity structure of a dynamic and heterogeneous system such as ours. While sensitivity analysis is an essential step to direct limited resources to the important uncertainty contributors for maximum reduction of uncertainty in model predictions, our method is particularly useful for grouping similar uncertainty contributors and identifying the most important group for additional parameter refinement. This sensitivity analyses strategy is currently being applied to a field hydro-biogeochemical conceptual model jointly developed by Task 2 and Task 5.

Task 5 has developed a new data assimilation method for delineating the spatial distribution of facies types conditioned on indirect data such as that from pumping tests. Our method integrates traditional transition probability-based geostatistics with ensemble-based data assimilation. The concept of “level set” allows application of ensemble-based data assimilation methods to estimate the distribution of discrete facies types, while the spatial structure of facies is determined by transition probability-based geostatistics using a set of conditioning points selected adaptively in the iterative process of data assimilation. This methodology has proved efficient and effective in a two-dimensional synthetic study that estimated facies spatial distribution and facies permeability from transient head data induced by pumping tests. It is now ready to be extended to field-scale facies-based modeling within the SFA project.

Task 5 has been working closely with Task 2 and 3 to build a conceptual model for hydro- and biogeochemical processes within the hyporheic zone at the local scale. The resulting model will also be used by Tasks 1 and 4. We have used modeling results to guide design of the piezometer network, and to identify the most promising temporal periods for data collection. Robust time series data from our hyporheic zone piezometer network collected through multiple dynamic hydrologic cycles is critically needed to define system behavior for model-data integration.

Task 5 has established a repository for our SFA data using open source PNNL software (Velo). The current capabilities include: preserving data with appropriate metadata, sharing data with the project team including external collaborators, a linked landing page for published data, integration with R studio for in-situ data analyses, and real-time viewing of images generated for data transmitted from the field by telemetry.

Plans for FY17

Data assimilation research will pursue three targets. 1) Extend the hierarchical sensitivity analyses method to field-scale, SFA hydro-biogeochemical models including climate scenarios. 2) Establish appropriate data assimilation methods to parameterize Task 3 enzyme-based kinetic models to ensure proper uncertainty propagation across scales. 3) Apply the facies-based data assimilation method to local and reach scale SFA hydrobiogeochemical models.

Select Science Highlights from Task Research

Task 1. Quantifying Hyporheic Exchange in a Large River Reach under Regulated Flow Conditions

Hyporheic exchange is an important hydrologic mechanism taking place in riverbank and riverbed sediment, where river water and shallow groundwater mix and interact with each other. The direction, magnitude, and residence time of hyporheic flux through the river bed are critical for carbon and nitrogen cycling, and the transformation of organic and inorganic contaminants. In this study, we combined field measurements and numerical modeling to estimate hyporheic fluxes across the river bed in a 7-km reach of the Columbia River. The reach features a minimum width of about 800 meters and great fluctuations (up to three meters) in river stage due to upstream dam operations. In shallow water along the shoreline, vertical thermal profiles measured by self-recording thermistors were combined with time series data of hydraulic gradient derived from river stage and in-land well water levels to estimate the hyporheic exchange rate. For the deeper waters, a high resolution computational fluid dynamics (CFD) modeling framework was developed to characterize the spatial distribution of flux rate on the river bed and the residence time of the hyporheic flux under different flow conditions. Our modeling results showed that the hyporheic flux and residence time of intruded tracer in river water were controlled by interactions between hydrostatic and hydrodynamic drivers induced by variations in river stage and flow velocity. Both drivers were modulated by river discharge as controlled by hydro-climatic conditions and reservoir operations which fluctuated across a wide range of time scales.

This study has resulted in one manuscript submitted to *Water Resources Research*. [See Zhou et al., 2016]

Task 2. Coupling Spatiotemporal Community Assembly Processes to Ecosystem Function

Community assembly processes govern shifts in species abundances in response to environmental change, yet our understanding of assembly remains largely decoupled from ecosystem function. Here, we test hypotheses regarding assembly and function across space and time using hyporheic microbial communities as a model system. We pair sampling of two habitat types through hydrologic fluctuation with null modeling and multivariate statistics. We demonstrate that dual selective pressures assimilate to generate compositional changes at distinct timescales among habitat types, resulting in contrasting associations of *Betaproteobacteria* and *Thaumarchaeota* with selection and with seasonal changes in aerobic metabolism. Our results culminate in a conceptual model in which selection from contrasting environments regulates taxon abundance and ecosystem function through time, with increases in function when oscillating selection opposes stable selective pressures. Our model is applicable within both macrobial and microbial ecology and presents an avenue for assimilating community assembly processes into predictions of ecosystem function.

The results have been published (https://doi.org/10.7287/peerj.preprints.2102v1) on the PeerJ pre-print server and are in review by the *ISME Journal*. [See Graham et al., 2016]

Task 3. Functional Enzyme Dynamics and Linkages with Biogeochemical Process Kinetics

Microbially mediated biogeochemical processes are regulated by enzyme activities that control the environmental transformations of carbon, nitrogen, and other elements. The dynamic linkage between functional enzymes and biogeochemical species transformation has, however, rarely been investigated because of the lack of analytical approaches to efficiently and reliably quantify enzymes and their dynamics in soils and sediments. We developed a signature peptide-based technique to quantify nitrate reducing enzymes in hyporheic zone sediments by applying targeted mass spectrometry. Enzyme concentrations were measured with high sensitivity and these correlated with the rates of nitrate reduction, consistent with inferred relationships from biogeochemical models based on biomass or functional genes as enzyme surrogates. However, enzyme concentrations continued to increase for several days after the exhaustion of nitrate as an electron acceptor, followed by an eventual decrease. This phenomenon was in contrast to predictions from biogeochemical models that enzyme abundance ceases to increase when the substrate is exhausted. The finding has important implications for the understanding of nitrate transformation dynamics, especially in environments with periodic nitrate fluxes. Our results demonstrate the importance of enzyme quantification for biogeochemical process identification and interrogation. They also provide basis for the development of function-based models to describe the evolution of microbial community functions and the associated kinetics of biogeochemical processes.

The results have been summarized in a manuscript submitted to *Proceedings of the National Academy of Science (PNAS)*. [See Li et al., 2016]

Task 4. Intercomparison Study of Pore-Scale Simulation Methods

Our multiscale modeling framework relies on the existence of well-developed single-scale models that can be coupled in a multiscale simulation. Although traditional continuum-scale flow and reactive transport simulators are quite mature, pore-scale simulators are a relatively recent development. An important aspect of our research is to expand and validate our world-class pore-scale simulation capabilities, to establish credibility for their predictive power and usability within our multiscale framework. To this end, we coordinated a multi-institution pore-scale model intercomparison study that compared several different methodologies and code implementations including traditional CFD codes, a Smoothed Particle Hydrodynamics (SPH) code, a Pore-Network Model (PNM) code, and a Lattice-Boltzmann (LB) code. The intercomparison was based on a previously published spherical bead pack column study in which pore geometry and pore-scale velocities were experimentally characterized using NMR methods. The results from all four model approaches compared favorably with one another and with experimental data, although some specific differences were observed primarily related to model discretization and boundary condition handling. The successful intercomparison study increases our confidence in pore-scale simulators, and provides a better understanding of the characteristics of the various methods as objective input to the model selection process.

The manuscript was invited for submission to a special issue of *Advances in Water Resource*s on the topic of “Pore-Scale Modeling and Experiments”. It has been accepted for publication and is currently available in Early View online (doi:10.106/j.advwatres.2015.09.015). [See Yang et al., 2015]

Task 5. A Geostatistics-Informed Hierarchical Sensitivity Analysis Method for Complex Groundwater Flow and Transport Modeling

Sensitivity analysis is an important tool for quantifying uncertainty in the outputs of mathematical models, especially for complex systems with a high dimension of spatially correlated parameters. Variance-based global sensitivity analysis has gained popularity because it can quantify the relative contribution of uncertainty from different sources. However, its computational cost increases dramatically with the complexity of the considered model and the dimensionality of model parameters. This study developed a hierarchical sensitivity analysis method that constructs an uncertainty hierarchy by analyzing the input uncertainty sources, and then accounts for the spatial correlation among parameters at each level of the hierarchy using geostatistical tools. The contribution of uncertainty from each level is represented by sensitivity indicies calculated using the variance decomposition method. Using this methodology, we identified the most important sources of uncertainty for a dynamic flow and transport model using field experimental data from a tracer experiment in the Columbia River subsurface interaction zone. The results demonstrated that boundary conditions and the permeability field contribute the most uncertainty to the simulated pressure field and tracer plume, respectively. The relative contribution from each source varied spatially and temporally as driven by dynamic interactions between groundwater and river water at the site. Furthermore, the method decreased computational cost to a manageable level by reducing the number of realizations using a geostatistical approach. The proposed sensitivity analysis method is generally applicable to a wide range of hydrologic and environmental problems that deal with high-dimension, spatially-distributed parameters.

The research has been submitted to *Water Resources Research* for publication [See Dai et al., 2016].

Future Scientific Goals, Vision, and Plans for Meeting Program Objectives

Our long term vision and grand challenge as presented in the FY 15 Science Plan still motivate our research. The specific short and long term goals for Triennial Period 1 will continue to be pursued through FY 17, as they are leading to impactful scientific findings and publications with important implications to the management of the Columbia River Basin. As stated in the FY 15 Science Plan: "the goals for TP-1 research (FY15-17) are to: *1) understand and model hydrologic, biogeochemical, and microbial ecologic process interactions at the local scale that regulate contaminant, carbon, and nitrogen fluxes across the subsurface interaction zone; 2) determine variations in subsurface interaction zone properties and characteristics throughout the Hanford Reach (including residence time, transit distance, and reaction rate) that control nutrient and contaminant fluxes between groundwater and surface water; and 3) initiate multiscale model development and analysis of subsurface interaction zone process interactions leading to improved reach scale predictions of targeted solute concentrations."* Beyond this we note that linked groundwater-surface water models, a current focus of PNNL SFA research, are increasingly recognized as an important need for regional Earth System Models, and for assessing the potential impacts of climate change, energy development, and agriculture on land surface hydrosystems.

The PNNL SFA Management team has begun preparations for our FY 17 Science Plan (Triennial Period 2) which is due to BER/CESD in February 2017. We have held two recent ½ day internal workshops on our TP-2 Research Plan with another planned in July. We have also been communicating with SBR management (David Lesmes and Paul Bayer) to identify evolving programmatic directions of the SBR program, and potentially impactful research that will best align with new CESD priorities. These planning activities will culminate in a briefing to be presented to CESD on the FY 17 Science Plan in September 2016. The FY 17 Science Plan will be led by Dr. Tim Scheibe as Principal Investigator, with Dr. James Stegen and Dr. Xingyuan Chen as Co-Principal Investigators. Dr. John Zachara will turn over management of the PNNL SFA to Tim Scheibe on Sept. 30, 2016. Dr. Jim Fredrickson will continue as a member of the P.I. team in FY 17, providing guidance and mentoring to the new leadership team.

Changes to the motivation and scope of Triennial Period 2 are anticipated given our initial dialogue with SBR management on the FY 17 Science Plan, and the staff changes noted above. While we will retain our focus on the hydrologic and biogeochemical workings of the subsurface interaction zone in the Columbia River Basin, SFA programs change as science needs and DOE priorities evolve. We envision the next update of our plan will include a new set of science questions that address new directions. These new directions will include high-level alignment with the Energy-Water Nexus and Integrated Water Cycle Workshop reports, as well as newer CESD concepts on impacts, adaptability, and vulnerability

(IAV) of watershed systems influenced by human activity and energy production. Our recent internal workshop, for example, considered broad water science issues facing the Columbia River Basin, as well as research opportunities and science questions associated with Columbia River hydropower generation, water diversion and irrigation return flow (as surface water and groundwater), and Columbia River impoundments. The FY 17 Science Plan will emphasize mechanistic process understanding of the groundwater - surface water interaction zone within the context of the overall watershed, and the development of biogeochemical models of managed systems that consider such topics as ecosystem function and resilience. The research will provide essential mechanistic underpinnings and improved linked ground and surface water models for watershed management and regional assessments of the Columbia River Basin with its extensive hydropower and irrigation infrastructure, and other large watersheds as well.

New Scientific Results that may Shift Current Research or Motivating Knowledge Gaps

The PNNL SFA has had difficulty obtaining high-quality time series data sets of water quality and hydrologic parameters from piezometers deployed in the hyporheic zone. Only one-of-three piezometer transects is delivering high quality data. Our scientific approach requires long term, time-series data (greater than two years) to define system behavior in response to hydrologic variation, and for model development, parameterization, and validation. Monitoring problems have resulted from the physical difficulties of piezometer installation in large river cobble; corrosion of metallic piezometer parts required for necessary strength; large hydraulic gradients resulting from dramatic river stage oscillations; erratic sensor responses and failure under challenging hydrodynamic conditions; and unexpected, spatially distributed, low permeability domains in the hyporheic zone.

These problems have led to a careful review of our monitoring strategies and a redesign of our piezometer systems and analysis methods. A new campaign of stainless-steel piezometer or aquifer tube installation oriented normal to the river axis will occur at several distinct locations during summer months as river water levels drop. Suitable high permeability locations will be identified by high resolution geophysical surveys. Sensors (dissolved oxygen, temperature, specific conductance, and pressure) will now be placed in different internal and/or external configurations to optimize performance given lessons-learned from previous deployments. Testing on new design options is beginning in July, 2016 as river stage drops to a manageable elevation. We anticipate the collection of high-quality time series data from multiple sites along the river corridor in the near future.

Collaborative Research Activities

The PNNL SFA currently has five collaborators who receive funds from the SFA project (see following section and Table 2). Their identities, organizational affiliations, and scientific contributions are as follows:

- Heping Liu, Washington State University – Install, maintain, and process data from eddy flux towers at multiple locations along the Hanford Reach for Task 1.
- Gautam Bisht, Lawrence Berkeley National Laboratory – Collaborate with Task 1 on linking CLM with PFLOTRAN, and test performance with various interaction zone and climate scenarios.
- Glenn Hammond, Sandia National Laboratory – PFLOTRAN developer, Task 2 modeling lead, and Task 1 and 4 modeling contributor.
- Eric Roden, University of Wisconsin – Task 2 biogeochemistry, investigating carbon sources driving microbial activity in the subsurface interaction zone.
- Ilenia Battiato, San Diego State University – Define facies-based applicability regimes for up-scaling fine scale geochemical and biochemical processes to the local and reach scale in Task 4.

Other Collaborations

1) The Multi-scale Synthesis and Terrestrial Model Intercomparison Project funded by NASA (MsTMIP, see at http://nacp.ornl.gov/MsTMIP.shtml) aims to quantify the contribution of model structural differences to computed estimates of land-atmosphere carbon exchange. The project involves a critical synthesis, benchmarking, and evaluation of models as necessary to improve the current state of the art in modeling the carbon cycle. The collaboration has resulted in two published journal articles. (Maoyi Huang, PNNL SFA collaborator)

2) The Regional Integrated Assessment Modeling Project funded by BER-IAR program (http://climatemodeling.science.energy.gov/projects/developing-regional-integrated-assessment-model-framework) aims to link regional climate, integrated assessment, energy, land, and hydrologic components to form a spatially flexible and temporally dynamic modeling framework. This project takes advantage of the Platform for Regional Integrated Modeling and Analysis (PRIMA) developed at PNNL. The SBR-SFA utilized models and datasets in PRIMA to simulate historic and future large-scale hydro-climatic conditions for the Columbia River Basin. The collaboration has resulted in one manuscript submitted to *Environmental Research Letters* and two manuscripts in preparation. (Maoyi Huang, PNNL SBR SFA collaborator)

3) The North America Land Data Assimilation System (NLDAS) Project (http://ldas.gsfc.nasa.gov/nldas/) funded by NOAA/NCEP's Environmental Modeling Center (EMC), NASA's Goddard Space Flight Center (GSFC), the NOAA/NWS Office of Hydrological Development (OHD), and the NOAA/NCEP Climate Prediction Center (CPC). The project is assembling high quality land-surface model (LSM) datasets to support modeling activities at 1/8th degree resolution over central North America. The collaboration has resulted in one manuscript submitted to the *Journal of Hydrometeorology* that evaluates groundwater modules in three advanced land surface models, including CLM. (Maoyi Huang, PNNL SBR SFA collaborator)

4) The development and testing of a multiscale modeling framework is being conducted in collaboration with the Interoperable Design of Extreme-scale Application Software (IDEAS) project. The IDEAS project is aimed at improving scientific productivity by addressing important trends emerging in extreme-scale scientific computing. Our SFA multi-scale modeling work draws on model coupling methodologies being developed under IDEAS (led by Mathew Thomas of PNNL), and provides feedback to IDEAS regarding the usefulness of the new software to our SFA-specific applications. (Tim Scheibe and Xiaofan Yang, PNNL SBR SFA collaborators)

5) An important aspect of our research is to expand and validate our advanced pore-scale simulation capabilities. The incorporation of multicomponent reaction chemistry and multiphase flow capabilities into the TETHYS pore-scale simulator is being conducted in collaboration with the Environmental Molecular Sciences Laboratory (EMSL). The multicomponent biogeochemical reaction code BIOGEOCHEM is being coupled with TETHYS and preliminary testing is being performed based on EMSL micromodel benchmark problems. Application of the upgraded code to 300A alluvial sediment core images will be performed by the SFA. (Tim Scheibe and Bill Perkins, PNNL SFA collaborators)

APPENDIX A: PROJECT PUBLICATIONS

2016

Barajas-Solano D. A. and Tartakovsky A. M. (2016) Hybrid multiscale finite volume method for advection-diffusion-reaction equations. *SIAM Journal on Multiscale Modeling*, In review.

Battiato I. (2016) Multiscale models of flow and transport. In *Handbook of Groundwater Engineering* (eds. J. H. Cushman and D. M. Tartakovsky). CRC Press, Accepted.

Bisht G., Huang M., Zhou T., Chen X., Dai H., Hammond G., Riley W., Downs J., Liu Y. and Zachara J. (2016) A fully coupled three-dimensional surface and subsurface land model for simulating groundwater and river water interactions at the field scale. *Geoscientific Model Development*, Submitted.

Bowen L., Tartakovsky A. M. and Battiato I. (2016) Macrodispersion induced by permeable surface topology. *Journal of Fluid Mechanics*, Submitted.

Dai H., Chen X., Ye M., Song X., and Zachara J.M. (2016) A geostatistics-informed hierarchical sensitivity analysis method for complex groundwater flow and transport modeling. *Water Resources Research*, Submitted.

Danczak R., Sawyer A. H., Williams K., Stegen J., Hobson C. and Wilkins M. J. (2016) Seasonal hyporheic dynamics control coupled microbiology and geochemistry in Colorado River sediments. *Journal of Geophysical Research: Biogeosciences*, Submitted.

Graham E. B., Crump A. R., Resch C. T., Fansler S., Arntzen E., Kennedy D., Fredrickson J. and Stegen J. (2016) Coupling spatiotemporal community assembly processes to ecosystem function. *The ISME Journal*, **4**, PeerJ Preprints: e2102v1, In review.

Ito A., Inatomi M., Huntzinger D. N., Schwalm C., Michalak A. M., Cook R., King A. W., Mao J. F., Wei Y. X., Mac Post W., Wang W. L., Arain M. A., Huang S., Hayes D. J., Ricciuto D. M., Shi X. Y., Huang M. Y., Lei H. M., Tian H. Q., Lu C. Q., Yang J., Tao B., Jain A., Poulter B., Peng S. S., Ciais P., Fisher J. B., Parazoo N., Schaefer K., Peng C. H., Zeng N. and Zhao F. (2016) Decadal trends in the seasonal-cycle amplitude of terrestrial CO_2 exchange resulting from the ensemble of terrestrial biosphere models. *Tellus Series B-Chemical and Physical Meteorology*, **68**, 28968; DOI: 10.3402/Tellusb.V68.28968. (from collaboration)

Johnson T. (2016) Decoupled modelling and inversion of complex conductivity data in the real number domain. *Geophysical Journal International*, Submitted.

Johnson T., Hammond G. E. and Chen X. (2016) PFLOTRAN-E4D: A parallel open source PFLOTRAN module for simulating time-lapse electrical resistivity data. *Computers and Geosciences*, Accepted;.

Korneev S. and Battiato I. (2016) Sequential homogenization of reactive transport in polydisperse porous media. *Journal of Computational Physics*, Submitted.

Leng G., Huang M., Voisin N., Zhang X., Asrar G. R. and Leung L. R. (2016) Emergence of new hydrologic regimes of surface water resources in the Conterminous United States under future warming. *Environmental Research Letters*, Submitted (from collaboration).

Li M., Gao Y., Qian W. J., Shi L., Liu Y., Nelson W. C., Nicora C., Resch C. T., Thompson C., Yan S., Fredrickson J., Zachara J. and Liu C. (2016) Quantification of functional enzyme dynamics and its linkage with biogeochemical process kinetics. *Proceedings of National Academy of Science, USA*, In review.

Liu Y., Xu F., Liu C. and Zachara J. (2016) Biogeochemical transformation of Cr, Fe, and O controlling Cr redox transformation and immobilization in the Columbia River hyporheic zone. *Water Research*, In review.

Mao J., Fu W., Shi X., Ricciuto D. M., Fisher J. B., Dickinson R. E., Wei Y., Shem W., Piao S., Wang K., Schwalm C. R., Tian H., Mu M., Arain A., Ciais P., Cook R., Dai Y., Hayes D., Hoffman F. M., Huang M., Huang S., Huntzinger D. N., Ito A., Jain A., King A. W., Lei H., Lu C., Michalak A. M., Parazoo N., Peng C., Peng S., Poulter B., Schaefer K., Jafarov E., Thornton P. E., Wang W., Zeng N., Zeng Z., Zhao F., Zhu Q. and Zhu Z. (2016) Disentangling climatic and anthropogenic controls on global terrestrial evapotranspiration trends. *Environmental Research Letters,* Submitted (from collaboration).

Renslow R., Lindemann S. and Song H. (2016) A generalized spatial measure for resilience of microbial systems. *Frontiers in Microbiology,* **7**, 443; DOI: 10.3389/fmicb.2016.00443.

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Song X., Ye M., Chen X., Dai Z., Hammond G. and Zachara J. (2016) Delineating facies spatial distribution by integrating ensemble data assimilation and indicator geostatistics. *Geophysical Research Letters*, Submitted.

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Stegen J. C., Konopka A., McKinley J., Murray C., Lin X., Miller M. D., Kennedy D., Miller E. A., Resch C. T. and Fredrickson J. (2016) Coupling among microbial communities, biogeochemistry, and mineralogy across biogeochemical facies. *Scientific Reports*, Accepted.

Sycheva L. V., Eggleston C. M., Magnuson T. S., Colberg P. J. S., Adam N., Zhang H. Z., Johnson P. and Shi L. (2016) Redox-linked conformation changes in adsorbed c-type cytochromes from *Shewanella oneidensis* MR-1 adsorbed to oxide surfaces. *Langmuir*, In review.

Tartakovsky A. M., Panzeri M., Tartakovsky G. D. and Guadagnini A. (2016) Uncertainty quantification in scale-dependent hydrogeological models. *Geophysical Research Letters*, Submitted.

Veach A. M., Stegen J., Brown S. P., Dodds W. K. and Jumpponen A. (2016) Spatiotemporal dynamics of stream biofilm microbes and the processes driving bacterial succession in a grassland stream ecosystem. *Molecular Ecology*, Accepted.

Wang Y., Pi K., Liu Y., Su C., Ma T., Li J., Liu C. and Xie X. (2016) Geochemical mechanisms of arsenic immobilization using in situ iron coating technology for managed aquifer rehabilitation. *Environmental Science & Technology*, Submitted (from collaboration).

Wu T., Griffin A. M., Gorski C. A., Shelobolina E. S., Xu H., Kukkadapu R. K. and Roden E. E. (2016) Interactions between Fe(III)-oxides and Fe(III)-phyllosilicates during microbial reduction 2: Natural subsurface sediments. *Geomicrobiology Journal,* In press.

Wu T., Kukkadapu R., Griffin A. M., Gorski C. A., Konishi C. A., Xu H. and Roden E. (2016) Interactions between Fe(III)-oxides and Fe(III)-phyllosilicates during microbial reduction 1: Synthetic sediments *Geomicrobiology Journal*, In press.

Xia Y., Mocko D., Huang M., Rodell M., Mitchell K. E., Cai X. and Ek M. B. (2016) Comparison and assessment of three advanced land surface models in simulating terrestrial water storage components over the United States: Preparation for next generation NLDAS system. *Journal of Hydrometeorology*, Submitted (from collaboration).

Xu F., Liu Y., Liu C., Zachara J. and Bowden M. (2016) Redox transformation and reductive immobilization of Cr(VI) in Columbia River hyporheic zone sediments. *Environmental Science & Technology*, Submitted.

Yan S., Liu Y. Y., Liu C. X., Shi L., Shang J. Y., Shan H. M., Zachara J., Fredrickson J., Kennedy D., Resch C. T., Thompson C. and Fansler S. (2016) Nitrate bioreduction in redox-variable low permeability sediments. *Science of the Total Environment*, **539**, 185-195; DOI: 10.1016/j.scitotenv.2015.08.122.

Zachara J., Brantley S., Chorover J., Ewing R. P., Kerisit S., Liu C., Perfect E., Rother G. and Stack A. G. (2016) Internal domains of natural porous media revealed: Critical locations for transport, storage, and chemical reaction. *Environmental Science & Technology*, **50**, 2811-2829; DOI: 10.1021/acs.est.5b05015.

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