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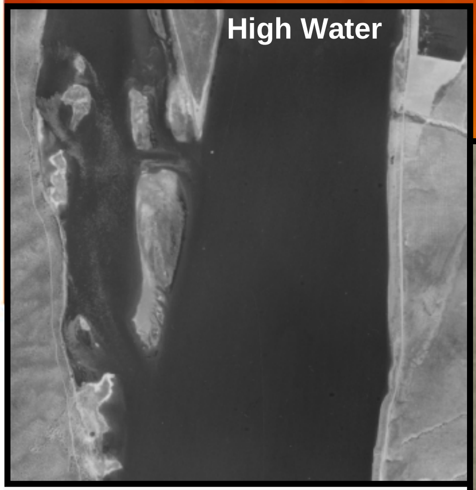

Pacific Northwest National Laboratory SFA Annual Report

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

June 2015

Laboratory Research Manager: Charlette Geffen

Principal Investigators: John Zachara (PI), Jim Fredrickson (Co-PI), and
Tim Scheibe (Co-PI)

Key Staff: Xingyuan Chen, Glenn Hammond, Jason Hou, Maoyi Huang, Chongxuan Liu, and James Stegen

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PNNL SBR Scientific Focus Area Annual Report FY2015

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

2015 Annual Report

June 30, 2015

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I. PROGRAM OVERVIEW

The transient movement of surface water to and through aquifer systems results in significant modifications to its 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 SIZ is a subsurface domain of temporally variable extent where groundwaters and surface waters mix in response to water cycle dynamics. 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 SIZ is a zone 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 SIZ serving as the last line of defense against the discharge of mobile, deleterious chemical agents to surface water. Consequently, a scientific understanding of the SIZ is absolutely fundamental to effective predictions of 1) contaminant fate and transport, and 2) C/N feedbacks to climate in coupled groundwater-surface water systems.

Because of the importance of the SIZ and associated biogeochemical processes to the sustainability of freshwater sources for the nation and the world, Pacific Northwest National Laboratory's (PNNL) Subsurface Biogeochemical Research (SBR) Scientific Focus Area (SFA) is addressing a grand research challenge focused on this critical, but poorly understood terrestrial interface. *PNNL's SFA will develop a predictive understanding of the groundwater-surface water interaction zone (termed subsurface interaction zone, SIZ) and its linkages with the water cycle that incorporates hydrologic impacts on fundamental biogeochemical and ecological processes into a multi-scale modeling framework that can be used to understand and predict system responses and feedbacks to natural or anthropogenic induced 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 and mission impact, while also building on past investments and scientific progress. Specifically, our research is being conducted on the closely linked unconfined aquifer-Columbia River system in Washington state, beginning at the Hanford 300 Area where uranium contamination exists, and expanding in the first 3-year period 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 representative of other large, gravel-dominated alluvial systems. Eight contaminant plumes (^{90}Sr, CrO_4^-, U, and NO_3^-) currently discharge through the interaction zone to the Hanford Reach with others expected in the future, while C and N partake in active hyporheic zone biogeochemical cycling leading to biogenic gas flux from the riparian zone and river. In the longer term, our work will be broadened to encompass the entire Columbia River basin, and extended to other impactful locations to validate our findings and models at the watershed scale.

We are addressing four, overarching science questions focused on reactive transport of contaminants, C, and N in pursuit of our grand research challenge.

1) What are the dynamics and spatial extent of the SIZ, what is the volume of river water processed through the SIZ, and how will these change in the future with non-stationary climate? How do biogeochemical processes in the SIZ influence river chemistry at the local and reach scales?
2) How do SIZ processes control and modulate the fluxes of contaminants (including near-shore plume persistence), C, and biogenic gases between groundwater and surface water? 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 contaminant transformations and biogeochemical processes in reactive transport models for robust prediction of the temporally and spatially dynamic, multiscale behavior of the SIZ?
4) What process hierarchies exist for the SIZ in moving from the local, to the reach, and to the catchment 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 SIZ in Earth system models?

III. NATIONAL LABORATORY PROGRAM STRUCTURE

The PNNL SBR 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. The contributing staff, including funded collaborators, are key disciplinary experts that work together in teams around major experimental or modeling campaigns to accomplish Task objectives and resolve hypotheses. Additional details on our management structure and philosophy are provided in our Science Plan.

The management and task structure of the PNNL SBR-SFA has remained fundamentally intact since the May 2014 review, with just one exception. At the beginning of FY 2015 we elevated our data management and assimilation activities to full task status (Task 5, Figure 1), with Dr. Xingyuan Chen functioning as Task lead. We believe this change will lead to stronger project support for CESD’s evolving data management activities.

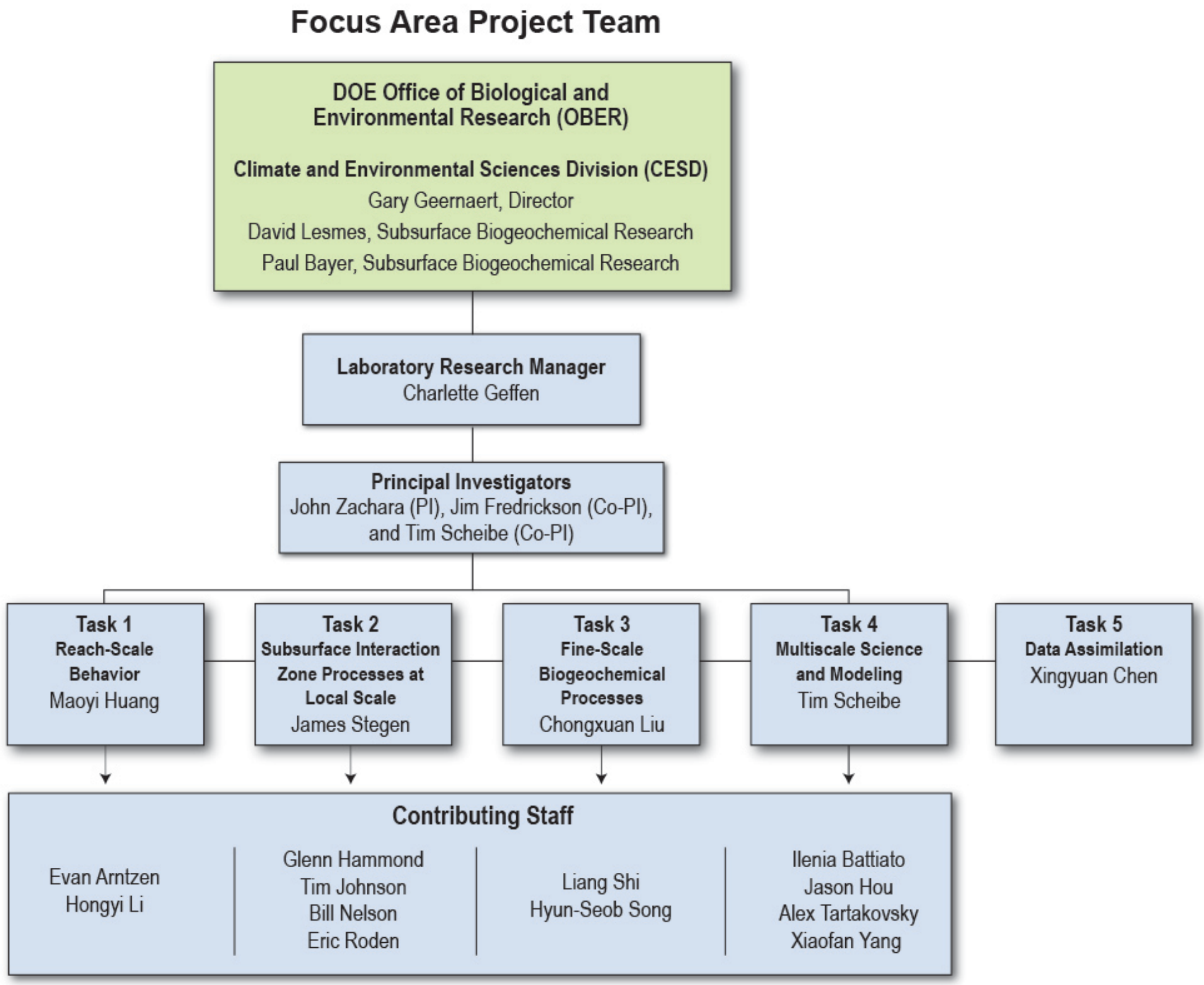

Figure 1. Focus Area Project Team.

IV. PERFORMANCE MILESTONES AND METRICS

Review of Scientific Progress Toward Program Objectives and Milestones

Task 1: Reach Scale Behavior

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 reach-scale 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 will contribute 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 concentrations/emissions from the subsurface interaction zone at the reach scale. Feedbacks to climate will 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).

FY15 Research Targets

The primary goals and research scope for FY 15 are to: 1) collect existing unique datasets on the Hanford Reach of the Columbia River, initiate new field measurements to identify locations of active groundwater-river exchange, and integrate into a reach-scale physical model; 2) begin development of the reach-scale facies model; and 3) configure and test the terrestrial and riverine models at the local scale.

Progress Brief for FY14-15

FY15 Science Plan Milestone: Collect existing unique datasets on the Hanford Reach, initiate new field measurements, and integrate into a reach-scale physical model. Begin development of the reach-scale facies model. Configure and test the terrestrial and riverine models at the local scale.

Existing data for the Hanford Reach have been collected to define a reach-scale physical model for use in multi-scale groundwater-surface water modeling activities. The data include: 1) hydrogeological measurements (riverbed and hyporheic zone particle sizes, physical/chemical/mineralogical properties); 2) riverine properties, such as river channel bathymetry derived from LIDAR measurements, river stage measurements, and riverbed substrate characteristics; 3) vegetation distribution from aerial surveys and physiological parameters/rooting profiles/allometry from ground-based ecological studies; 4) thermal imagery data for low river stage periods to identify springs, preferential flow channels, and agricultural returns; and 5) historical meteorological data.

Plans were developed for riparian and vadose zone monitoring to provide land surface gas (CO_2, CH_4, N_2O) flux measurements for reach scale projections. Actions considered were: i) monitoring vadose zone soil moisture and pore gas composition along transects normal to the river channel in the riparian zone, and ii) installation of multiple eddy covariance systems in the Hanford River Corridor to measure water, energy, momentum, and gas exchanges between land and atmosphere. Permit requests have been submitted to the appropriate authorities for both of these activities with the expectation that they will be initiated in late FY15.

Conceptual models for the coupled land surface-subsurface-river system along the Hanford Reach were evaluated under the CLM-PFLOTRAN framework. Initially, standalone CLM and CLM-PFLOTRAN simulations were run at 2, 10, and 20 m resolutions over a 400m × 400m domain in the 300 Area, where the most complete dataset was available from previous natural experiments performed by Task 2. The models were constrained by site-specific land cover, soil parameters, and local meteorological data. The PFLOTRAN vertical domain was extended from the soil surface to the Hanford-Ringold contact, using subsurface properties from previous PFLOTRAN modeling at the site. The lateral boundary conditions for CLM and PFLOTRAN were provided by groundwater monitoring wells and observed river stages. Three-month long CLM-PFLOTRAN simulations for the summer of 2012 were performed with the coupling of hydrologic processes between CLM-PFLOTRAN to test code performance. Multi-year simulations with CLM-PFLOTRAN are now being performed to better understand the impact of river water and groundwater interactions on surface and subsurface hydrologic states and fluxes under different climate and hydrologic conditions.

The riverine model, MOSART, has been configured for the Columbia River over different spatial domains to initiate our upscaling activities from the local to reach scale. These include the Hanford Reach at 1 km resolution, a selected 1 km segment at 100m resolution, and a100 m segment at 20 m resolution Numerical stability has been achieved at each resolution. This nested multi-resolution implementation of the code demonstrates that MOSART can be applied at various spatial resolutions across both the local and reach scales. Calibration of MOSART parameters against observed river stages and annual discharge profiles is now being performed to ensure that the real-world behavior of the river has been sufficiently incorporated within MOSART to satisfy CLM-PFLOTRAN's requirements for boundary conditions.

Plans for FY16

Key targets for future reach scale research are to: 1) finalize data collection and assemble the initial reach-scale facies model, including identified areas of groundwater river-exchange determined by boat-based, high resolution thermal imagery, 2) analyze Hanford Reach eddy flux data to determine the influence of soil moisture variability, groundwater discharge, and environmental variables on the surface energy budget and land/water biogenic gas fluxes, and 3) enhance coupling between CLM, PFLOTRAN, and MOSART to include thermal, biogeochemical, and mass transfer processes to assess the spatial and temporal dynamics of biogeochemical cycling and biogenic gas generation in the interaction zone, and their regulation by water cycle and climate variations.

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 will contribute 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.

FY15 Research Targets

The primary goals and research scope for FY 14-15 are to: 1) evaluate the influence of groundwater-surface water mixing on biogeochemical solutes, ecological processes, microbial community composition, metabolic potential, respiration, and biomass; 2) identify the source(s) of organic carbon that fuel microbial metabolic activity in the interaction zone and the microbe-driven transformations that occur as organic carbon moves through this zone; 3) characterize the effects of surface water intrusion on the temporal dynamics of surface-atmosphere exchange of biogenic gases; 4) describe the spatial structure and biological/physical/biogeochemical/hydrologic properties of local sediment facies; and 5) track hydrologic mixing dynamics and couple these dynamics—using data assimilation—with a local-scale flow and transport model enhanced with explicit biogeochemical reactions.

Progress Brief for FY14-15

FY15 Science Plan Milestone: Identify local-scale interaction zone characteristics, properties, and processes (physical, hydrologic, and geochemical) that control microbial community structure and biogeochemical activity in time and space.

Aqueous field samples collected in a spatiotemporal design revealed that groundwater-surface water mixing results in a coupled response among ecological processes, microbial communities, and biogeochemical rates. Field studies indicated a time-scale-dependence of ecological processes, with deterministic processes dominating at longer time-scales. Additional field efforts that focused on substrate-associated microbial communities revealed that microbial respiration and biomass were strongly influenced by spatial position within the interaction zone. A non-linear effect of groundwater-surface water mixing was observed on dissolved oxygen concentrations within the hyporheic zone, but little influence was noted across the broader subsurface interaction zone. High resolution characterization of dissolved organic matter, in collaboration with EMSL, indicated substantial differences in the composition of carbon from different sources influencing microbe-driven carbon transformations. These carbon analyses indicate sizeable differences between labile and refractory carbon pools.

An initial freeze-coring effort accessed the hyporheic zone along a transect parallel to river flow. This effort enabled identification of local scale facies based on grain size analyses. Current research is evaluating relationships between facies-specific grain size distributions and parameters associated with microbial communities and biogeochemical function. A second effort co-located high-spatial-resolution geophysical characterization with hydraulic testing, and freeze-coring. This effort revealed marked spatial variation in the vertical structure of local-scale facies and their hydraulic properties. Freeze-cores are currently being processed to characterize spatial variation (vertical and horizontal dimension) in physical, microbial, and biogeochemical parameters. In addition, 4-dimensional geophysical monitoring of groundwater-surface water mixing was initiated near the river shoreline to improve understanding of mixing dynamics within the hyporheic zone. Both the high-spatial-resolution and near-shore geophysical monitoring were designed to improve parameterization of a local scale hydro-biogeochemical model.

Laboratory experiments performed on field-incubated substrates indicate that dissolved organic matter in the river water column was not the cause of stimulated microbial activity in the hyporheic zone which occurs in response to groundwater-surface water mixing. An initial experiment found that river-derived carbon did not stimulate microbial respiration; microbial respiration was instead determined by the location (in the field) where experimental substrates were incubated. This experiment also indicated that microbial respiration in the upper layer of riverbed sediments may be partially decoupled from temporal fluctuations in organic carbon inputs. Preliminary evidence from a follow-on experiment suggests that hyporheic microbial community respiration is stimulated by organic carbon derived from riverbed sediments, as opposed to carbon derived from the river water itself. If verified, this result can be used to improve the local-scale hydro-biogeochemical model by providing a quantifiable source term for organic carbon, which appears to drive biogeochemical rates across the interaction zone.

Several other important activities have been initiated. Field sampling was performed to characterize the effects of surface water intrusion on the spatial structure and temporal dynamics of surface-atmosphere exchange of biogenic gases. This effort involved geospatially informed sampling of CO_2, CH_4, and N_2O using soil chambers, and high temporal resolution sampling of CO_2 and CH_4 using field deployed auto-chambers. Shotgun metagenomic sequencing is underway as part of our JGI-EMSL user proposal. Included are 17 samples derived from substrates incubated in the hyporheic zone across different spatial locations and a broad range of groundwater-surface water mixing conditions. High resolution carbon characterization—also under the JGI-EMSL proposal—is being applied to freeze-core sediments from multiple potential facies types. Variation in carbon composition and the quantity and type of microbial transformations will be related to physical, biological, and biogeochemical properties of the facies. Extension of PFLOTRAN is underway to include biogeochemical reaction networks identified and quantified by Task 3, and a variable mesh size to provide higher resolution in the near-shore hyporheic zone. Field efforts summarized above provide physical, hydrologic, and aqueous biogeochemical data needed to calibrate and evaluate this version of PFLOTRAN.

Plans for FY16

Key targets for future local scale research are to: 1) characterize the multi-scale structure of physical properties, biogeochemical processes, and microbial community composition and function existing across the groundwater-surface water interaction zone; 2) develop and validate 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.

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 SIZ; 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 will contribute to 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 biogeochemical transport models will be developed for field and multiscale integration and applications.

FY15 Research Targets

The primary goals and research scope for FY 14-15 are to: 1) characterize redox properties of newly collected sediments from the subsurface interaction zone and determine their capacities for contaminant transformation and biogenic gas production, 2) evaluate and optimize approaches to quantify the abundance of functional genes and enzymes in sediments using microbial denitrification as an example; and 3) develop numerical model frameworks for describing microbial community functions in linking with biogeochemical reactions and water flow.

Milestone and Progress Brief for FY14-15

FY 15 Science Plan Milestone: Identify sediment characteristics and spatiotemporal variation of redox-active domains that control contaminant migration and gas production (CO_2, N_2O, and CH_4) in subsurface interaction zone sediment facies. Infer reactions and reaction network from laboratory experiments and sediment characterization.

Sediments from Columbia River shoreline were collected at representative locations in collaboration with Task 2. These were characterized to determine redox processes catalyzing Cr reduction and re-oxidation, and microbial community functions with respect to denitrification coupled to organic carbon degradation. Chromate [Cr(VI)] was rapidly reduced by the Columbia River hyporheic zone sediments, and reduced Cr(III) was stable upon exposure to O_2-containing water. The results implied that hyporheic zone sediments have potential to remove Cr from contaminated groundwater entering the river system. Ongoing research will quantify parallel abiotic and biotic reduction pathways, and will identify the mineral association of precipitated Cr(III) in the sediments. A manuscript is targeted by the end of FY15.

Initial laboratory results indicated that the microbial community in hyporheic zone sediments can reduce nitrate through microbial denitrification as regulated by a set of functional genes and enzymes. Research was consequently initiated to develop and optimize measurement approaches to quantify the abundance of the functional genes and enzymes involved in denitrification that exist in the sediment at low concentration. Linkage of the functional gene and protein concentration dynamics during denitrification with the macroscopic biogeochemical reaction rates is critical to develop and test genome-informed biogeochemical models of the transformation of carbon, nitrogen and contaminants in the subsurface interaction zone.

Two complimentary metabolic model frameworks were developed to describe the system-scale behavior of microbial community functions that integrate the dynamics of functional genes/enzymes with observed biogeochemical reaction rates. One model was based on the cybernetic concept and the other on maximum system entropy production. Both models treat the microbial community as a complex system, with biogeochemical reactions as the system functions. The individual reactions and rates are regulated by functional enzyme activities, and the system-scale behavior is described by control theories. A manuscript has been written and submitted as a proof of concept. Both models will be evaluated against denitrification data being collected in ongoing laboratory experiments with hyporheic zone sediments to determine which is most tractable, versitile, and robust for project-wide application.

Other research initiated during this time period includes: 1) characterization of organic carbon speciation and solid/liquid partitioning in hyporheic zone sediments to understand the migration and reactivity of organic carbon during groundwater and surface water interactions; 2) pore-scale modeling of denitrification and organic carbon degradation to provide insights into the effect of fine-scale facies, biofilms, or physical and biogeochemical heterogeneity on effective reaction rates; and 3) column experiments to investigate the reactive transport of C and N under dynamic hydrologic conditions mimicking groundwater and surface water exchange in the hyporheic zone.

Plans for FY16

Key targets for future fine-scale research are to: 1) develop a Cr redox transformation model including biotic and abiotic reactions and the effects of fine-scale facies properties on parameter values and upscaling; 2) investigate dissolved and particulate organic carbon speciation, transformation, and secondary reaction during denitrification and establish comprehensive reaction networks; 3) determine the dynamics of functional genes and enzymes during and after denitrification to establish an enzyme growth and decay model; and 4) validate and refine metabolic models by comparison to SFA laboratory experimental data from subsurface interaction zone sediments.

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 specify 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.

This task fills an integrative role in addressing the SFA Research Grand Challenge, in that development of a predictive understanding of the subsurface interaction zone (SIZ), a complex natural system, requires incorporation of mechanistic understanding from fine-scale studies into larger-scale (field and reach scale) models. This task is developing and testing the overall multiscale modeling framework within which each of the other SFA task models are to be integrated.

FY15 Research Targets

The primary goals and research scope for FY 14-15 are to: 1) develop hierarchical facies definitions at fine, local, and reach scales; 2) define facies-based applicability regimes for upscaling fine-scale processes; and 3) identify multiscale modeling methods for linking fine- and local-scale models of reactive transport at the Hanford 300 Area.

Progress Brief for FY14-15

FY15 Science Plan Milestone: Develop hierarchical facies definitions at fine, local, and reach scales (with Tasks 1-3). Define facies-based applicability regimes for upscaling fine-scale processes (diffusion-limited U mass transfer, with Tasks 2 and 3) and identify multiscale modeling methods for linking fine- and local-scale models of U reactive transport at the 300 Area.

Facies definitions and characterization: Multiple data types (bathymetry, river substrate, grain size, thermal imagery, microbial/geochemical attributes of freeze core samples) with various spatial coverage and resolution, have been collected, cataloged, processed, and analyzed for the purpose of identifying multiscale facies and understanding their control on biogeochemical properties. In the context of reactive transport modeling, we aim to define classes of riverbed sediment that are distinct both in terms of the primary observable properties (e.g., grain size, mineralogy) that form the facies definition, and in secondary properties (e.g., biogeochemical reactivity) that are important to model predictions. Folk-

Wentworth geological classification was used to group grain-size distribution data from 21 freeze cores (Task 2) into four base lithofacies. Hierarchical clustering analysis was also performed on the 21 samples, using a combination of microbial/geochemical and grain size attributes to identify biogeochemical facies and evaluate their relationship to grain-size based lithofacies.

To be useful for predictive modeling, facies must be mappable at the relevant model scales. We are exploring a variety of surrogate data that has broad spatial coverage that may be related to facies type. Maps of facies classifications will be used to assign spatial distributions of model parameters through the statistical relationships established between facies type and biogeochemical/physical properties. Surrogate data that can be used to map facies include: 1) geophysical surveys at the local field scale, which can delineate the geometry (thickness) of the riverbed sediment layer; 2) river bathymetry from LIDAR measurements, available through the Hanford Reach; and 3) reach-wide data on riverbed substrate properties (e.g., dominant grain size class for each sampled location). Tools have been developed to extract spatial statistics from bathymetric and riverbed substrate data that can be tested for correlations with facies type at locations where direct measurements of grain size are available.

Facies-based applicability regimes for upscaling fine-scale processes: A key feature of our multiscale approach is the combination of traditional upscaling methods, where appropriate, with more complex hybrid multiscale methods when required. We are extending earlier applicability regime research based on homogeneous porous media to more realistic systems in which subsurface media are made up of multiple facies, each with different grain size distributions and pore structure. Several of the Hanford Reach facies are characterized by large gravel clasts with a finer-grained matrix, so as a first step we have performed combined theoretical and numerical analysis of media with two dominant length scales. Because the applicability conditions are formulated in terms of dimensionless parameters (e.g., Peclet and Damkohler numbers) that incorporate a characteristic length scale, selection of the appropriate length scale in heterogeneous systems is a critical challenge. Pore-scale simulations are being used to numerically evaluate conditions under which upscaled models break down, and then compared to theoretical results to identify appropriate length scale definitions.

Multiscale modeling framework development: We are developing and testing a hybrid multiscale modeling framework that facilitates the coupling of two or more simulation codes operating at distinct scales. The framework is designed for use in a high-performance computing environment, and implements the Heterogeneous Multiscale Method formalism within the SWIFT workflow environment, with customized python scripts providing the linkages necessary for data exchange. We have successfully applied this framework to a mixing-controlled reaction problem, linking pore- and continuum-scale models within a single simulation. We are currently applying the framework to simulate groundwater and river water exchange, with associated denitrification, at the 300 Area local field study site.

The framework relies on the existence of well-developed single-scale models that can be coupled in a multiscale simulation. Although traditional continuum-scale simulators are quite mature, pore-scale simulators are a relatively recent development. One aspect of our work is to continue to expand and validate our advanced pore-scale simulation capabilities, to establish credibility for their predictive power and usability within our multiscale framework. Another aspect focuses on simulation of uranium surface complexation and associated aqueous speciation reactions; the coupling of the new module with TETHYS has been completed and the code system is being verified using a series of increasingly complex test problems. We have successfully applied the TETHYS code to simulate a laboratory column experiment of sufficient size to allow us to draw conclusions about continuum-scale phenomena based on explicit pore-scale process understanding. We have also conducted a multi-code, multi-method pore-scale model intercomparison study involving traditional CFD codes, a Smoothed Particle Hydrodynamics (SPH) code, a Pore-Network Model (PNM) code, and a Lattice-Boltmann (LB) code.

Plans for FY16

Key targets for future multiscale science and modeling research are to: 1) define facies mapping techniques at the local scale based on surrogate measures, 2) integrate 3D riverbed and aquifer facies distributions and denitrification reaction networks from Task 3 into the multiscale simulation framework and test against measurements (Task 2), 3) use the newly developed pore scale model of U surface complexation to evaluate applicability conditions, and embed in the hybrid simulation framework for field-scale simulations of U transport in the groundwater-surface water interaction zone, and 4) identify a suitable multiscale modeling approach for the Hanford Reach with Task 1, and begin parameterizations of necessary processes and properties such as volumes of interaction zone exchange and residence times.

Task 5: Data Assimilation

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 model predictability 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.

FY15 Research Targets

Our goals and research scope for FY 14-15 are to: 1) develop data assimilation capability for characterizing the heterogeneous permeability field at the groundwater-surface water interface (hyporheic zone) using time-lapse electric resistivity tomography (ERT) datasets; 2) provide the characterized permeability field to the hydro-biogeochemical modeling in Tasks 2 and 4 and CLM-PFLOTRAN simulations in Task 1; and 3) initiate efforts to establish a central data repository for the PNNL SBR-SFA that fully complies with DOE/BER policies on publishing datasets and dissiminating project data to the scientific community.

Progress Brief for FY14-15

FY15 Science Plan Milestone: New Task, no milestones identified in Science Plan.

Ensemble-based data assimilation methods have been developed and tested for integrating time-lapse ERT data to characterize aquifer hydrologic properties in the interaction zone, thus providing essential property fields for hydro-biogeochemical modeling in Tasks 2 and 4 and coupled CLM-PFLOTRAN simulations in Task 1. The method has been further enhanced to enable facies-based data assimilation which is now being tested using new measurements and data from local and fine scale research. Task 5 has also initiated efforts to establish our SFA data repository using open source, PNNL software (Velo). Leveraging investments by the PNNL IT department, we will enhance Velo capability to facilitate publication of project data sets compliant with DOE’s digital data policy.

Plans for FY16

Key targets for data assimilation research are to: 1) incorporate data reduction and data worth analysis to identify most valuable components of any data set to be assimilated for SFA modeling activities, 2) use sensitivity analysis to assess the impacts of uncertainty in petrophysical models, the location of the Hanford-Ringold contact, and flow boundary conditions on hydrogeophysical data assimilation, 3) apply facies-based data assimilation methods to hydrogeophysical data assimilation, and 4) build a structured project data repository with facile search and publishing capability.

Select Science Highlights from Task Research

1. *Groundwater and River Water Interactions Modulate Land Surface and Subsurface States and Fluxes: A Local-Scale Case Study along the Columbia River Shoreline*

An integrated land surface and subsurface model enhanced with hydrologic exchange was assembled within the land component of an ESM (i.e., the Community Land Model (CLM) coupled with PFLOTRAN) to investigate how land-atmosphere exchange is influenced by the lateral flow and mixing of waters within the groundwater-surface water interaction zone. The new model (along with stand-alone codes as reference) was applied to a domain including 400 m of the Columbia River shoreline where subsurface properties and processes have been well-documented through sediment characterization, pump tests, tracer experiments, and field monitoring of river water intrusion events driven by river stage changes. Initial objectives were to: 1) investigate the impact of land surface and subsurface heterogeneity (including topography, vegetation, and permeability) on land and subsurface fluxes and state variables and 2) assess the impact of temporal variability in precipitation and river stage on the volume and duration of groundwater-surface water exchange, and subsequent land-atmosphere interactions. Simulations of CLM-PFLOTRAN at multiple spatial scales were conducted using observed meteorological and river stage data under different climate and hydrologic conditions. The coupled model revealed the importance of interaction zone processes in regulating temporal and spatial variability in land surface and subsurface fluxes and state variables. River water intruded into the subsurface with increasing river stage which increased soil moisture for evapotranspiration and suppressed available energy for sensible heat transfer. Higher spatial variability in near surface soil moisture was observed in CLM-PFLOTRAN simulations because of the explicit inclusion of subsurface heterogeneities in hydrologic properties. These initial results revealed that strong coupling may occur between land surface and subsurface processes and fluxes in riparian zones. These results should be validated by field measurement, with improved process understanding considered in next generation ESM.

The results are summarized in two manuscripts being submitted to *Geoscientific Model Development* and the *Journal of Advances in Modeling the Earth System*.

2. *Groundwater-Surface Water Mixing Shifts Ecological Assembly Processes and Stimulates Organic Carbon Turnover*

Environmental transitions often result in resource mixtures that overcome limitations to microbial metabolism, resulting in biogeochemical hot spots and moments. Riverine systems where groundwater mixes with surface water (the hyporheic zone) are spatially complex and temporally dynamic, making development of predictive models challenging. Spatial and temporal variations in hyporheic zone microbial communities are a key, but understudied component of riverine biogeochemical function. To investigate the coupling among groundwater-surface water mixing, microbial communities, and biogeochemistry we applied ecological theory, aqueous biogeochemical measurements, DNA sequencing, and ultra-high resolution organic carbon profiling to field samples collected across times and locations representing a broad range of groundwater-river mixing conditions. Mixing of groundwater and surface water resulted in a shift from transport-driven stochastic dynamics to a deterministic microbial structure associated with elevated biogeochemical rates. While the dynamics of the hyporheic zone make predictive modeling a challenge, we provide new knowledge that can improve the tractability of such models.

The results have been submitted to *Nature Communications.*

3. Effective Reaction Rates Vary in Heterogeneous Porous Media

The scaling behavior of an effective reaction rate law under variable water flow conditions was investigated in physically heterogeneous porous media. Subgrid domain-based approaches were evaluated to scale redox reaction rates from the pore to continuum scales. The continuum assumption is typically adopted in defining and modeling reactive transport processes in subsurface environments. A micromodel system with heterogeneous pore structures was developed for measuring and simulating pore- and continuum- scale variations in reaction rates under variable water flow conditions. Numerical analysis revealed complex scaling behavior of redox reaction rate laws and associated parameters from the pore to continuum scales. An important conclusion was that it is not feasible to robustly scale reaction rates from the pore to continuum scales without knowledge of the detailed pore structure of the media. However, continuum models properly embedded in subgrid domains can largely eliminate the scaling effect. The research implied that reaction rate laws and constants will be scale-dependent in heterogeneous subsurface materials, being affected by flow velocity, and the variations in physical and chemical properties in the different subgrid domains. Models containing embedded subgrid domains provide a realistic and numerically efficient way to directly scale geochemical and biogeochemical reactions in heterogeneous subsurface materials.

The results are in press in *Geochimica et Cosmochimica Acta*.

4. Demonstration and Testing of a Hybrid Multiscale Modeling Framework

We developed a multiscale framework for coupling two codes at different scales into a unified hybrid simulation. The framework was applied to two test problems. The first problem was a mixing-controlled reaction between two solutions flowing in parallel. Our work demonstrated that the hybrid coupling of pore- and continuum models led to improved prediction of the mass of reaction product generated without resorting to empirical fitting of the apparent reaction rate (the currently accepted approach). The second problem was multiscale coupling of PFLOTRAN simulations of flow and biogeochemical reactions (denitrification) at the 300 Area. The small-scale model resolves sub-meter facies variations (flow and biogeochemical parameters) within the riverbed sediments and near-river zone while the large-scale model extends the results over a much larger (400x400 meter) domain extending inland at the 300 Area. Preliminary coupling of the two model scales has been used to successfully simulate oscillatory flows associated with river water stage elevation changes.

The results of the first test case have been accepted in *Advances in Water Resources*. A description of the coupling framework approach, together with discussion of test case applications, has been published in *Procedia Computer Science*.

5. Coupled Hydrogeophysical Data Assimilation for Characterizing the Groundwater-Surface Water Interface

Accurate characterization of sediment permeability at the aquifer-riverbed interface is critical for understanding and modeling associated hydro-biogeochemical processes and fluxes. The distinct contrast in aqueous specific conductance between river water and groundwater along the Columbia River shoreline allows for application of a cost-effective geophysical technique (electrical resistance tomography, ERT) to image complex and dynamic river water intrusion events over sizable spatial domains. We used measurements from a large-scale ERT array (300 m by 300 m) to estimate the underlying subsurface permeability field extending from the hyporheic zone to the inland aquifer using ensemble-based algorithms (e.g., ensemble Kalman filter and ensemble smoother). A new high-performance multi-process code that couples flow and transport (PFLOTRAN) with ERT imaging (E4D) provided the key modeling capability of multi-physical processes, parallel efficiency, and multi-realization simulation capability for hydrogeophysical data assimilation. We divided the rich ERT dataset into spatial and temporal segments and assimilated them sequentially to deal with the high data dimensionality. Our study demonstrated the effectiveness of joint hydrogeophysical data assimilation for characterizing aquifer properties in the groundwater-river interaction zone. The use of high performance computing (Hopper at NERSC) was indispensable for stochastic assimilation of rich spatial-temporal data using our complex multi-physics model.

The results have been submitted to *Water Resources Research.*

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

The PNNL SFA submitted a new Science Plan to CESD in Feb. 2014 for FY 2015-2017 that was subjected to panel peer review in May 2014. The Plan presented a nine year vision involving three triennial periods for grand challenge research on the groundwater – surface water interaction zone. Specific shorter term scientific goals, plans, and milestones were described for FY 2015, FY 2016, and FY 2017 (Triennial Period 1, TP-1). The Plan was accepted by CESD without change in Sept. 2014, and PNNL began implementing the Plan on Oct. 1, 2014. At the time of writing this report (June 1, 2015) PNNL has been performing research described in the new Science Plan for 8 months, with progress as described above.

Our long term vision and shorter term scientific goals and plans remain unchanged, and those presented in the Science Plan still motivate our research. As stated in the 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."*

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

One motivating hypothesis in our Science Plan was that riverine dissolved organic matter (DOM), imported into the subsurface interaction zone during periods of high river stage, would be the primary energy source driving biogeochemical activity. However, recent field observations suggest an alternative hypothesis: that particulate organic C in hyporheic zone sediments resulting from primary productivity and associated high dissolved organic C in hyporheic zone porewaters drive biogeochemical activity in the interaction zone. This finding will change our carbon characterization strategy, and necessitate additional experimentation to discern the physical forms of particulate organic matter in the hyporheic zone, processes controlling its desorption and reactive transport, and the specific identity of carbon substrates that drive reaction networks with biogeochemically active solutes (contaminants and nutrients). These changes have been implemented in our evolving Science Plan.

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 one published journal article. (Maoyi Huang, PNNL SFA collaborator)

2) 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. IDEAS is aimed at improving scientific productivity by addressing important trends emerging in extreme-scale scientific computing. While scientific objectives create increasing demands for predictive multiscale and multiphysics simulations, rapid changes in hardware and software limit the effectiveness of traditional software development approaches. IDEAS promotes an efficient and agile approach to software engineering focused on community engagement in a software ecosystem composed of high-quality, reusable components and libraries. The scope of IDEAS includes multiscale simulation and model coupling activities applied to two major use cases, one of which is focused on hyporheic exchange and biogeochemistry in meander bends of the East River in the upper Colorado River basin (analogous to our 300A denitrification test

case). The SFA work draws on model coupling methodologies being developed under IDEAS (led by Kirsten Kleese-van Dam of PNNL), and provides feedback to IDEAS regarding the results of our test case application. (Tim Scheibe and Xiaofan Yang, PNNL SFA collaborators)

3) A collaborative demonstration project was undertaken jointly by members of the PNNL and LBNL SFA projects and other key collaborators at those two institutions. In this work, the Akuna-Agni platform (from the ASCEM project) was customized to simulate land surface fluxes using the Community Land Model (CLM). Two demonstrations have been completed: a) 1D CLM simulations of the NGEE-Arctic site, with sensitivity analysis performed on several soil parameters (e.g., organic content, percent clay and sand), and b) 1D CLM simulations of the ARM Southern Great Plains site, with sensitivity analysis of ten parameters and application of the parameter estimation toolset. We are working toward demonstrations of 3D CLM simulations at the NGEE-Artic and Hanford 300 Area sites. (Tim Scheibe and Maoyi Huang, PNNL SFA collaborators)

APPENDIX A: PROJECT PUBLICATIONS

2015

Barajas-Solano, D. A., and A. M. Tartakovsky (2015), Hybrid multiscale finite volume method for advection-diffusion-reaction equations, *SIAM Journal on Multiscale Modeling*, In review.

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