*PNNL-SA-83343*

# HANFORD IFRC QUARTERLY REPORT ~ October 2011

**John M. Zachara and the IFRC Research Team**
***Pacific Northwest National Laboratory***

## I. Management Statement

In this October 2011 Quarterly Report for the Hanford IFRC project, we summarize activities performed during the fourth quarter of FY 2011. The primary emphasis of fourth-quarter research has been: i.) completion of upper aquifer hydrologic testing, ii.) continued data assimilation with the objective to develop petro-physical models for the interpretation of IFRC 3D geophysical measurements; iii.) modeling the March 2010 and 2011 desorption experiments; iv,) completing multi-investigator laboratory experimentation for the smear zone reactive transport model; and v.) pre-modeling the planned October 2011 high U injection experiment.

At the time of this reporting 100% of the FY has elapsed and 98.3% of our total FY 2011 IFRC budget has been spent, including 3rd party commitments [e.g., allocations to University participants and Central Hanford Plateau Remediation Co. (CHPRC) for well drilling and completion]. The IFRC project carried over $350K of FY 2010 funds that were used for the installation of four new wells for hydrologic modeling control points, and for well-field remediation. The Hanford IFRC is ahead on spending because of costs incurred during well-field mitigation, effectiveness documentation, and hydrologic characterization of the upper high K zone of the U plume.

The IFRC and SFA management teams have also been discussing future research plans for the IFRC site, including scientific approaches to extend IFRC research to the system or plume scale. Our initial ideas on this subject were presented to SBR management in August 2011. These ideas include:

- Expanding the research domain beyond the current IFRC site to include a larger region that is representative of the system, including linking paleo-channels and the active zone of groundwater-river interaction, mixing and exchange.
- Changing the research theme from multi-scale mass transfer to contaminant dynamics, microbial ecology, and biogeochemistry in the groundwater-river interaction zone.
- Placing greater emphasis on system characterization and monitoring, system-scale process delineation and modeling, and uncertainty reduction through a prior-posterior data assimilation and modeling approach.

Planning the future direction of the IFRC will continue over the first and second quarters of FY 2012, and we are excited about our evolving approach. This plan, however, is contingent on funding levels and gaining access to Hanford site 300 Area monitoring wells. Monitoring well access was once easy, but issues have arisen with union labor that has traditionally performed this activity for the Hanford site. We have initiated dialog with the DOE-RL site steward to identify the process and procedures for accessing these wells for research purposes.

## II. Select Highlights

- Hydrologic characterization has been completed on the mitigated well-field. Electromagnetic borehole flow-meter measurements have been completed at 15 cm depth increments, and constant rate injection tests have been performed in all new wells. These measurements yield vertically discretized values for hydraulic conductivity that are being assimilated into an updated geostatistical model of hydraulic conductivity for the upper aquifer that is being used to model the spring 2011 desorption experiment. This new data set shows significant differences in hydraulic conductivity distribution for the upper aquifer than implied from earlier measurements performed over the entire aquifer depth. We have seen no evidence for vertical well-bore flows in any of the mitigated wells.

- We continued to make progress in re-analyzing the March 2009 experiment using the revised EBF (flow-meter) profiles. In our last quarterly report we compare two IFRC well-field cross sections developed using the previous and the current flow-meter (EBF) profiles. This quarter we can report some preliminary, positive results from this analysis.

  Our analysis includes the implementation of the MAD algorithm (developed for this project) to the moments of the breakthrough curves from the March 2009 experiment and the revised EBF profiles. The nearby figures demonstrate the improvement in our ability to predict the breakthrough curves. The results for 2-27 show that the prior and posterior means are quite close, which suggest (for now) that the re-testing of the EBF profiles played an

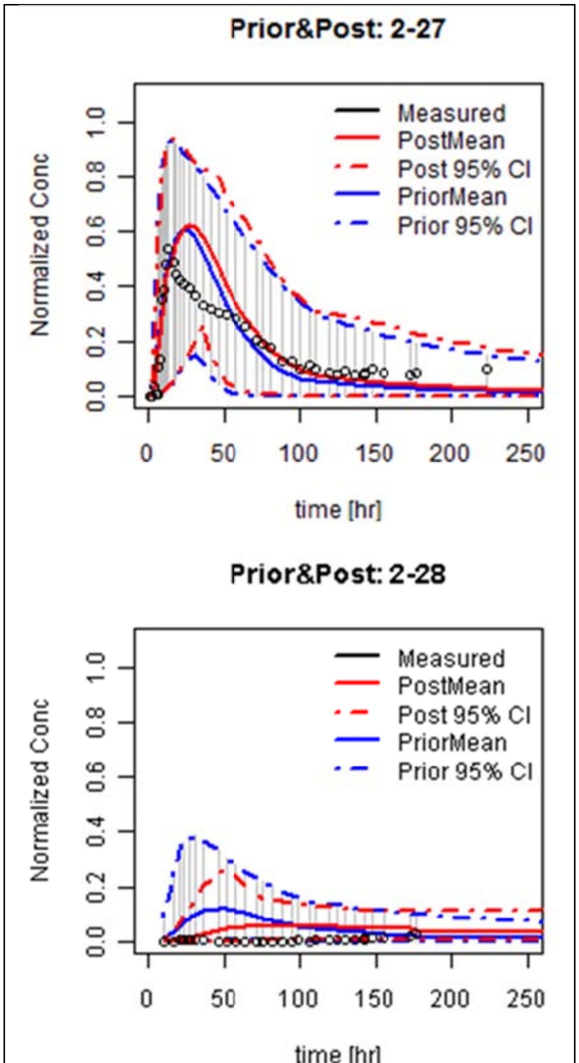


**Figure 1**. Prior and posterior mean breakthrough curves in wells 2-27 and 2-28 and their 95% confidence intervals (CI). Open circles represent measured breakthrough curves. These plots are based on results from the re-analysis.

important role in getting this improvement. Significant remaining discrepancies for 2-28 indicate continued uncertainty in hydraulic conductivity distribution in select regions of the well-field.

- Monitoring of the stable isotope compositions of groundwater from the IFRC well field has been conducted since the beginning of the March 2011 U desorption tracer test in collaboration with Los Gatos Research (LGR) scientists (Elena Berman and Manish Gupta) who are funded through a Small Business Innovative Research (SBIR) grant to demonstrate the utility of the LGR automated water isotope analytical system. To date, ~2500 samples have been analyzed, providing a high-quality data set on variations in the isotope compositions of groundwater in the IFRC well field.

  During the March/April tracer test conducted at the site, $D_2O$ was added to the last tank of tracer solution for comparison with the NaCl (which was added to all four tanks of tracer solution injected into the groundwater). During the test, unusually high precipitation in the Columbia River watershed led to unseasonably high water levels in the river. This resulted in changing directions of groundwater flow in the IFRC plot which was captured by the movement of the chloride tracer, but confounded by multiple passes of the same water through the well field. Tracking of the deuterium allowed discrimination of the last tracer aliquot from the net effect of all four aliquots.

  Isotope monitoring of the well field groundwater continued through peak river stage in late spring/early summer. The isotopic composition of groundwater is distinctive from Columbia River water, enabling use of the isotope data to quantify the proportion of river water infiltrating into the well field during high river stage. Since the isotope compositions are conservative tracers, they can be compared to shifts in chemical data to estimate the effects of processes such as ion exchange or mineral dissolution on the groundwater composition. River water fractions calculated from the conductivity are significantly lower, presumably due to mineral-water reactions occurring during transport from the river to the monitoring well (Figure 2).

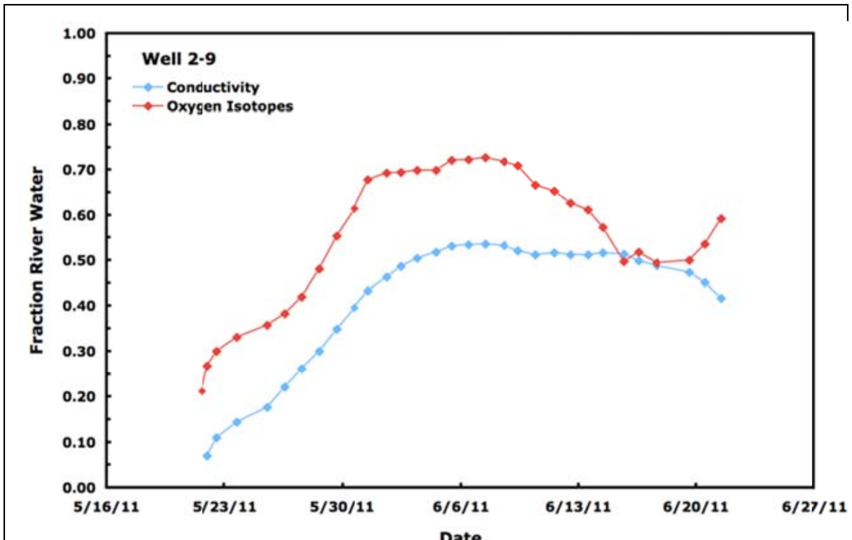


**Figure 2**. The fraction of Columbia River water in IFRC well 2-9 during the spring high-water event as calculated from shifts in the $\delta^{18}O$ and the specific conductance of well-water.

- A multi-investigator team has been

investigating U desorption behavior from a site-wide smear zone composite with the objective of developing a kinetic geochemical model that can be linked with our field transport simulators. The OSU team (Yin and Haggerty) have conducted two sets of column experiments to evaluate potential U(VI) fluxes out of the smear zone at the Hanford IFRC Site. The < 8 mm IFRC side-wide composite sediment was packed into two columns with identical lengths (46.8 cm) and inner diameters (4.28 cm). Synthetic Hanford Groundwater (SGW) was injected upward into the bottom of the columns to desorb U(VI). In one of the columns, pore water was gravity drained from the bottom before conducting two extended stop-flow events, with the sediment re-saturated at the end of stop-flow events.

Samples collected from the top of both columns showed very similar U(VI) concentrations during the pumping and after the stop-flow events. Sample differences in major ions, pH and alkalinity were also small. However, U(VI) concentrations are an order of magnitude lower in gravity-drained samples collected at the bottom of the column than in the samples collected from the top through pumping (Figure 3b). The low concentrations in the gravity-drained samples were maintained throughout the whole drainage event, while around 22.4% and 18.1% of pore water was drainble in two events within 24 hrs.

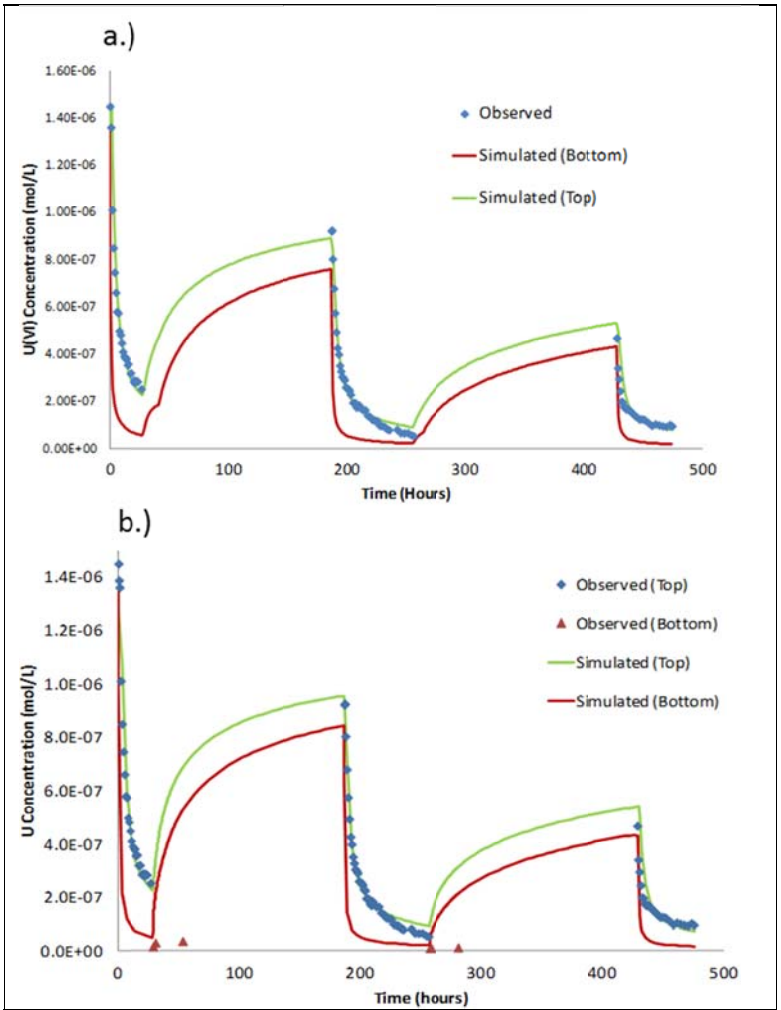


**Figure 3**. Observed and simulated U(VI) desorption in two column experiments: **a**) fully saturated experiment two saturated stop-flow events; b) saturated flow experiment with two unsaturated stop-flow events. The observed U(VI) concentrations at the bottom of the column are flux-averages.

A multi-rate surface complexation model embedded in STOMP was used to simulate the observed U(VI) desorption. The site-wide composite sediment was characterized through batch experiments at USGS (Stoliker & Kent), and the parameters were used as initial values in the model calibration. The model was first calibrated against the observed U(VI) in the effluent from the column with saturated stop-flow events (e.g., 3a). The calibrated model was then used to simulate the U(VI) transport in the column with drainage events and unsaturated stop-flow.

The calibrated model precisely captured the observed U(VI) increase during the stop-flow events in both columns (Figure 3). The same surface complexation reaction and kinetic rate distribution were apparently valid for rate-limited U(VI) desorption under both saturated and unsaturated conditions. The simulation results also revealed that the U(VI) pore-water concentration at the bottom of the column near the point of SGW inflow should be much lower than the U(VI) concentrations in waters that exit from the top of the column. Therefore the observed low U(VI) concentrations in the drainage waters were reflective of conditions in the lower portion of the column. When pumping was stopped during the stop-flow event, U(VI) desorbed at the same kinetic rate throughout the entire column.

Although U(VI) desorption may be different when the matric potential in the sediment is very low [ongoing experiments seek to quantify this], the in-situ saturation conditions in the IFRC smear zone are closer to the relatively high water contents of these column experiments. Accordingly, when the field sediment is saturated by the rising groundwater with low U(VI) concentration, a vertical gradient in pore-water U(VI) concentration may evolve with lower U(VI) at the bottom of the smear zone. The U(VI) pore-water concentration in this zone will increase with duration of saturation due to rate-limited U(VI) desorption. When the water table lowers, total U(VI) fluxes at the bottom of the smear zone depend largely on the frequency of the groundwater table oscillations, as well as on the time period that the smear zone sediment was saturated.

These results and model parameters are now being integrated with others from the research team, and with the geostatistical model for U distribution, to establish a comprehensive model of smear zone behavior that can be used to simulate passive and injection experiment results that are impacted by fluxes from this zone.

- A U desorption field experiment was performed in March to April 2011. The experiment injected low U groundwater at slow rate into the upper aquifer of the remediated well field (10 gpm; 220,000 gallon total) for an extended period (15.3 d). The objective was to create a narrow plume through the center of the well-field where aquifer sediment was depleted in adsorbed U. We expected that the advancing front of returning native groundwater would display retardation as depleted adsorption sites were refilled by U in higher concentration site groundwater.

  Unfortunately, unpredicted heavy rains began soon after the initiation of the experiment that caused a surge in Columbia River discharge that impacted the performance of the experiment. While our data set is robust and comprehensive, it is complex displaying the effects of multiple reversals in groundwater flow direction and advance of the water table into the U-enriched smear zone before the traditional period of water table advance. We have begun to model the breakthrough data with PFLOTRAN that includes a stochaistic representation of the hydraulic conductivity field (Figure 4). This conductivity field has not been updated with our recently completed hydrologic measurements and improvements are soon expected. The model includes rate-limited surface complexation in the saturated zone, but no source or sink terms in the smear zone.

As revealed in Figure 4, the breakthrough data for the individual wells was complex, displaying concentration spikes and dips. This behavior was a result of the oscillatory river stage behavior that caused our narrow plume to swing back and forth across the IFRC well field, intersecting different wells at different times. Certain wells intersected and sampled the plume at multiple times during the dynamic experiment. Modeling has captured this dynamic behavior nicely for certain upper aquifer wells (e.g., 2-07 and 2-26). U behavior in cluster wells below the injection domain (2-27 and 2-28) were not well described, although the deviation for deep well 2-27 results from a different initial U condition in that well that was not factored into the modeling analysis. An additional noted discrepancy between data and model was the rebound concentration after passage of the tracer/desorption plume. The initial concentration in the upper aquifer was 42 ug/L, while the rebound concentration in wells 2-24, 2-07, 2-09, 2-11, and 2-26 ranged from 50-55 ug/L and decreased with time after approximately 600 h. This increase in the rebound concentration over the

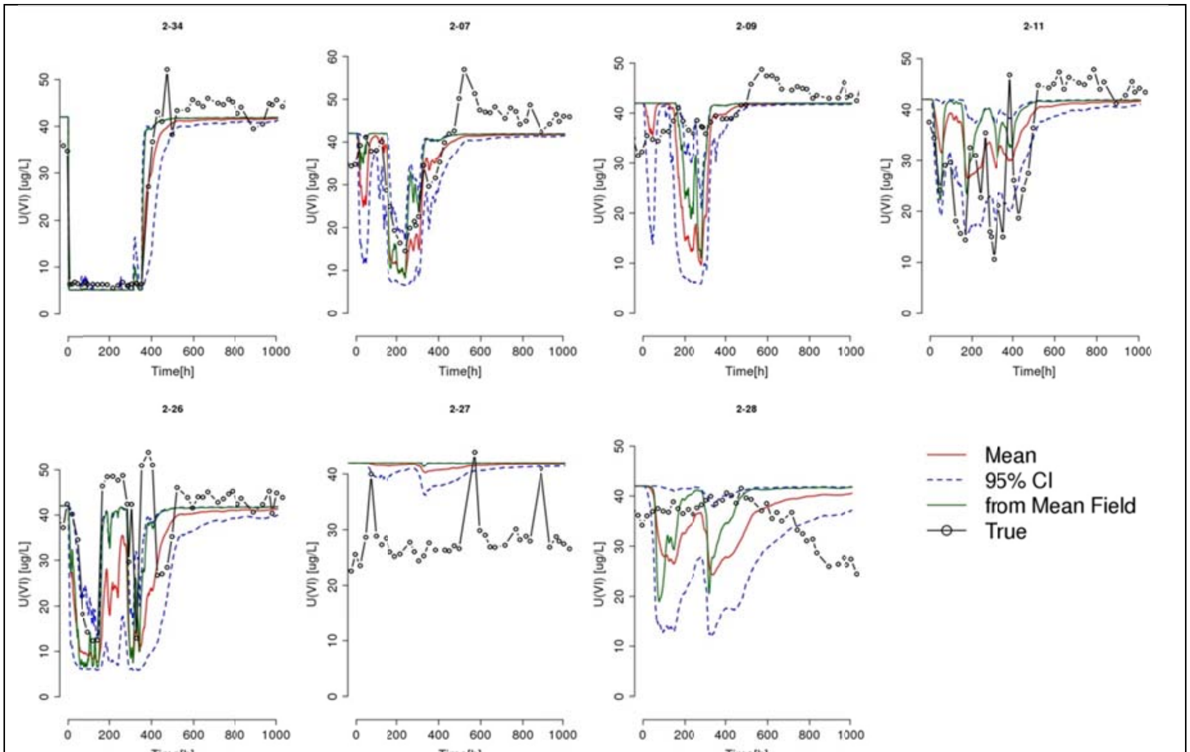


**Figure 4**. Model simulations of U(VI) breakthrough behavior in selected wells during the March-April 2011 desorption experiment. The initial groundwater condition was 42 ug/L U(VI). The injected groundwater contained 6 ug/L.

initial concentration resulted from the excursion of the water table in the lower smear zone approximately 200 h into the experiment. U release from the smear zone is not yet accounted for in the site model. An important finding of the experiment was that the extent of adsorptive U retardation was much less than that estimated from laboratory studies of intact saturated zone cores. Indeed, there was no discernable retardation of returning groundwater U.

## III. Plans for Next Quarter

A major objective for next quarter is the performance of a series of injection experiments during low water in October 2011 using the high U groundwater concentrate that was collected in July 2011. It will be our first experiment using excess concentrations of U. The 40,000 gallons of groundwater concentrate with 1800 ug/L U(VI) has been stored on site in two tank trucks. We have received permit approval to reinject, and have recently completed a test plan for the experiment. The experiment will involve three phases. The groundwater concentrate will be diluted to 600 ug/L, a representative value for enriched U-fluids emanating from the smear zone during spring high water. The 120,000 gallons will be used in three sequential injections:

1.) A 600 ug/L injection (100 gpm) in native groundwater to the upper aquifer.
2.) A 600 ug/L injection (100 gpm) in “river water” to the upper aquifer.
3.) A 600 ug/L injection (25 gpm) to the low K intermediate zone.

The “river water” experiment will provide insights on the in-situ transport of U that is mobilized in the spring by intruding river water. Currently under debate is whether Richland domestic water (treated river water) or untreated river water will be used. The debate centers around microbiologic issues and whether a cost- and staff-effective sampling and analysis plan could be assembled to investigate the transport and survival of riverine organisms in the rapidly migrating plume.

The experimental design has been support by an extensive PFLOTRAN modeling campaign using hydrologic conditions anticipated for October 10 – November 10. Example pre-modeling results are shown in Figure 5 for an assumed injection concentration of 600 ug/L in native groundwater in well 2-34. Pre-modeling predicts very little retardation of the 600 ug/L plume. Note superposition of gold [U(VI)] and black ($Br^-$) breakthrough curves Pre-modeling is underway for the river water injection where more retardation is expected because of its lower pH, and bicarbonate and $Ca^{2+}$ concentrations.

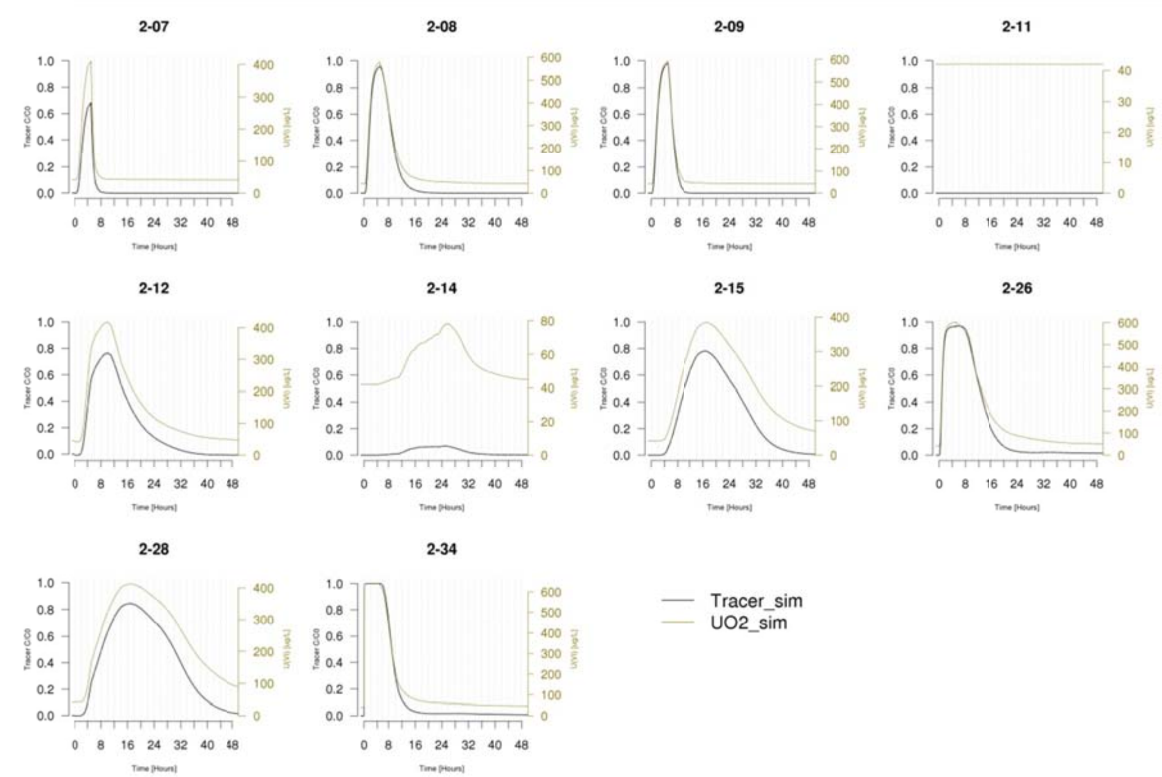


**Figure 5**. Premodeling the injection of 600 ug/L U(VI) in native groundwater into the IFRC site. Output is provided for non-reactive tracer $Br^-$ and contaminant U.

## IV. Fourth Quarter Publication Acivity

Greskowiak, J., M. B. Hay, H. Prommer, C. Liu, V. E. Post, R. Ma, J. A. Davis, C. Zheng, and J. M. Zachara. 2011. Simulating adsorption of U(VI) under transient groundwater flow and hydrochemistry – physical versus non-equilibrium models. *Water Resources Research 47,* w08501, doi:10.1029/2010wr010118.

Hay, M. B., D. L. Stoliker, J. A. Davis, and J. M. Zachara. 2011. Characterization of the intragranular water regime within subsurface sediments: Pore volume, surface area, and mass transfer limitations. *Water Resources Research* (Accepted).

McKinley, J. P., J. M. Zachara, C. T. Resch, R. M. Kaluzny, M. D. Miller, V. R. Vermeul, B. G. Fritz, and J. V. Moser. 2011. River water intrusion and contaminant uranium contributions to groundwater during the annual spring rise in Columbia River stage at the Hanford Site 300 Area, Washington. *Environmental Science and Technology* (Submitted).

Murray, C. M., J. M. Zachara, J. P. McKinley, A. Ward, K. Draper, and D. Moore. 2011. Establishing a geochemical model for a contaminated vadose zone – aquifer system. *Journal of Contaminant Hydrology* (Submitted).

Nowak, W., Y. Rubin, and F. P. J. de Barros. 2011. A hypothesis-driven approach to optimal site investigation. *Water Resources Research* (Accepted).

Shang, J., C. Liu, and J. M. Zachara. 2011. Grain-size dependent kinetics of uranium(VI) adsorption and desorption and rate additivity. *Environmental Science and Technology* 45, 6025-6031.

Stoliker, D. L., D. B. Kent, and J. M. Zachara. 2011. Application of surface complexation modeling to evaluate difference in equilibrium uranium(VI) adsorption properties of aquifer sediments. *Environmental Science and Technology,* doi/org10.1021/es202677v.