Cleaning up the cold war: simulating uranium migration at the Hanford 300 Area

Glenn Hammond,[1] Peter Lichtner[2]

[1]Hydrology Group, Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA, 99352
[2]Hydrology, Computational Earth Sciences Group, Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, NM, 87545

E-mail: glenn.hammond@pnl.gov and lichtner@lanl.gov

Abstract. The reactive multiphase flow and geochemical transport code PFLOTRAN, developed under the SciDAC-2 program, is employed to simulate groundwater flow and uranium [U(VI)] contaminant transport at the Hanford 300 Area. Simulations predict that ~25 kg/yr of U(VI) leach into the neighboring Columbia River. Simulations further predict that heterogeneous permeability, modeled through stochastically-generated random fields, has little impact on the flux of U(VI) to the river.

1. Introduction

Throughout the Cold War, facilities at the Hanford site in south central Washington State were built and utilized to produce plutonium in support of nuclear weapons production. During this period of time, many regions of the Hanford site were contaminated with waste byproducts resulting from the nuclear weapons production process. Cleanup operations at the Hanford site have been ongoing since the close of the Cold War in the mid-1980's, but many of the contaminants at the site still exist in the subsurface. In particular, at the Hanford 300 Area, where nuclear fuel rods were fabricated, uranium [U(VI)] has persisted in the underlying aquifer far longer than the original estimates for natural attenuation [1,2]. These erroneous estimates resulted from uncertainty regarding the extent of the source zone(s), which remains uncertain, and the use of an overly simplistic process model for U(VI) sorption (i.e., the KD model) [3]. In order to better understand the persistence of U(VI) at the Hanford 300 Area and its leach rate into the neighboring Columbia River, variably-saturated groundwater flow and multicomponent geochemical transport simulations are being employed to simulate U(VI) migration at the site using the massively-parallel, reactive multiphase flow and geochemical transport code PFLOTRAN [4]. PFLOTRAN is currently being developed under the Department of Energy Office of Science SciDAC-2 program to advance scientific understanding of subsurface processes and improve predictive flow and transport capability. In these PFLOTRAN simulations, high-performance computing is employed to preserve numerical accuracy through high-resolution computational grids and accommodate the large number of chemical species and small time steps needed to accurately depict river-groundwater interaction.

In the sections that follow, the Hanford 300 Area is described in further detail, along with the governing equations employed within PFLOTRAN and the Hanford 300 Area conceptual model. Estimates of the U(VI) flux to the Columbia River are then presented for several conceptual models of soil permeability and U(IV) sorption at the site.

2. Background

The Hanford 300 Area is located in the southeast corner of the Hanford site along the western bank of the Columbia River, just north of the city of Richland, Washington as shown in Figure 1. Facilities at the 300 Area were used to fabricate nuclear fuel rods for plutonium production during the Cold War. During fuel rod production, U(VI) was discharged into several process ponds (i.e., the North and South Process Ponds) and nearby trenches. This U(VI) infiltrated into the underlying soils and aquifer contaminating the groundwater in the region. Over time, this contaminated groundwater has migrated towards the river, slowly seeping into the river through the hyporheic zone at the river bottom.

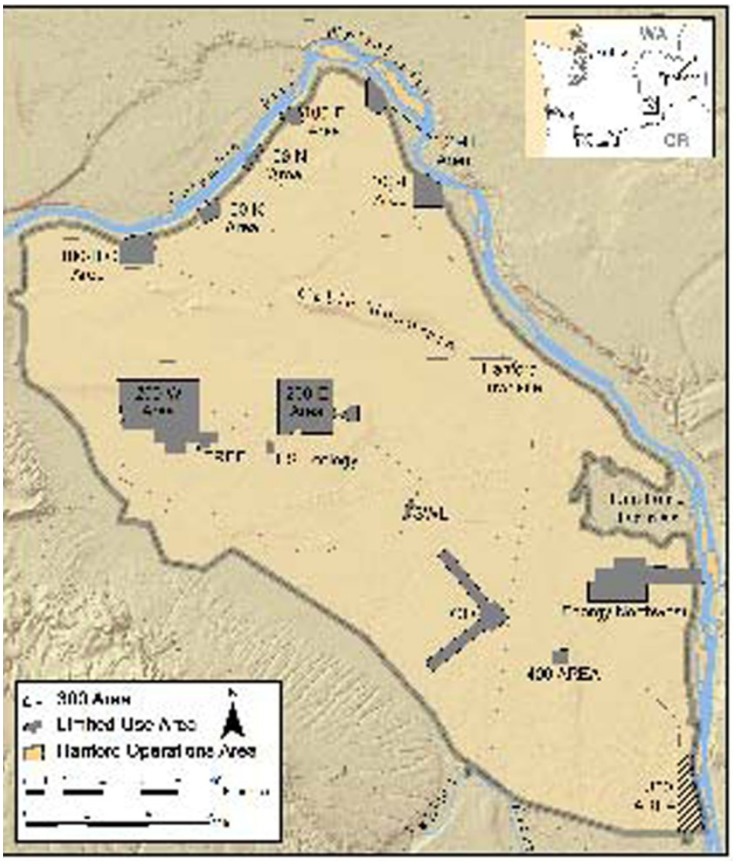

Figure 1. Map of the Hanford Site showing the location of the Hanford 300 Area to the lower right.

The undulating Columbia River stage plays a dominant role in controlling groundwater flow within the aquifer underlying Hanford 300 Area. River stage fluctuates ~2.5 meters annually due to seasonal variation with daily fluctuations of up to ~1.5 meters due to cyclic spillage from the Priest Rapids dam upriver. Due to the high permeability of aquifer materials, water flows readily in and out of Hanford 300 Area aquifer when river stage is high and low, respectively. Thus, the river stage drives cyclic groundwater flow and consequently the migration of the U(VI) plume at the site. However, sorption of U(VI) to soil grains is so strong that the contaminant travels much slower than the groundwater pore velocities.

The real challenge posed by the U(VI) plume at the 300 Area is its persistence due to sorption onto aquifer materials. Regulators desire that groundwater concentrations be reduced from current levels of over 100 μg/L to below the maximum contaminant limit (MCL) of 30 μg/L for U(VI). Although this reduction in concentration will surely occur as a result of natural attenuation of U(VI) as it slowly leaches in to the river, the time frame of natural attenuation is uncertain; the plume could persist for

decades to centuries. Assuming that the 300 Area will be remain a brown field (i.e., off-limits to the public) for years to come, the question then becomes what is the flux of U(VI) to the river over the course of a year and is this U(VI) flux acceptable? Although the latter question is for regulators to decide, quantification of the U(VI) flux to the river is possible through simulation of groundwater flow and geochemical transport using PFLOTRAN.

3. Governing Equations

The conceptual model employed in this work for simulating U(VI) migration at the Hanford 300 Area incorporates groundwater flow in both the vadose and saturated zones and multicomponent geochemical transport (i.e., aqueous speciation, surface complexation, and mineral precipitation-dissolution). The PFLOTRAN governing equations for single-phase variably saturated groundwater flow and geochemical transport in porous media are detailed below.

3.1. Variably-Saturated Flow

PFLOTRAN's variably-saturated flow equations based on the Richards equation [5] have the form

$$\frac{\partial}{\partial t}(\varphi s \rho) + \boldsymbol{\nabla} \cdot \rho \boldsymbol{q} \;=\; 0, \tag{1}$$

with water density ρ, porosity φ, water saturation s, and Darcy velocity $\boldsymbol{q}$ given by

$$\boldsymbol{q} \;=\; -\frac{k k_r}{\mu} \boldsymbol{\nabla} (p - \rho g z), \tag{2}$$

with pressure p, viscosity μ, acceleration of gravity g, intrinsic permeability k, relative permeability k_r, and z the component of the distance vector aligned with gravity. The van Genuchten relation [6] is used to relate capillary pressure to water saturation and the Burdine correlation [7] is used for relative permeability.

3.2. Geochemical Transport

PFLOTRAN's multicomponent reactive transport equations have the form

$$\frac{\partial}{\partial t}\left(\varphi s \Psi_j + \Psi_j^S\right) + \boldsymbol{\nabla} \cdot \boldsymbol{\Omega}_j \;=\; -\sum_m \nu_{jm}^{\min} I_m. \tag{3}$$

In this equation the quantity Ψ_j denotes the total aqueous concentration of the jth primary species

$$\Psi_j \;=\; C_j + \sum_i \nu_{ji}^{\mathrm{aq}} C_i, \tag{4}$$

where the concentration of the ith secondary species C_i is expressed as a function of primary aqueous species activities through the mass action equation

$$C_i \;=\; \frac{K_i}{\gamma_i} \prod_j \left(\gamma_j C_j\right)^{\nu_{ji}^{\mathrm{aq}}}, \tag{5}$$

with equilibrium constant K_i, stoichiometry ν_{ji}^{aq} and activity coefficients $\gamma_{i,j}$

The quantity Ψ_j^S denotes the total sorbed concentration of the jth primary species

$$\Psi_j^S \;=\; \sum_{k\sigma} \nu_{jk}^{\mathrm{srf}} S_{k\sigma}, \tag{6}$$

where $S_{k\sigma}$ denotes the surface complex concentration of the kth species for site σ. PFLOTRAN supports both equilibrium and multirate kinetic formulations of surface complexation. However, for brevity only the equilibrium formulation is described in this work. The multirate formulation is

described in detail by [8]. For equilibrium surface complexation, concentrations of surface complexes $S_{k\sigma}$ and empty surface sites $S_{\chi\sigma}$ satisfy the site conservation equation of the form

$$\omega_\sigma = S_{\chi\sigma} + \sum_k S_{k\sigma}, \tag{7}$$

for sorption site σ. The site concentration ω_σ [mol sites/m^3] is related to the specific site surface density η_σ [mol sites/m^2] of the medium by the relation

$$\omega_\sigma = \eta_\sigma A_\sigma \rho_r (1-\varphi). \tag{8}$$

In this equation the quantity η_σ denotes the moles of surface sites of type σ per unit area, A_σ represents the specific sorptive surface area in units of m^2/g, and ρ_r refers to the rock grain density. The concentrations for unoccupied sites $S_{\chi\sigma}$ and surface complex $S_{k\sigma}$ are found to be

$$S_{\chi\sigma} = \frac{\omega_\sigma}{1+\sum_k K_k Q_k}, \tag{9}$$

and

$$S_{k\sigma} = \frac{\omega_\sigma K_k Q_k}{1+\sum_{k'} K_{k'} Q_{k'}}, \tag{10}$$

where the ion activity product Q_k is given by

$$Q_k = \prod_j (\gamma_j C_j)^{\nu_{jk}^{\mathrm{srf}}}. \tag{11}$$

The total solute flux Ω_j is defined by

$$\mathbf{\Omega}_j = \left(\boldsymbol{q} - \varphi s \tau D \boldsymbol{\nabla}\right)\Psi_j, \tag{12}$$

with tortuosity τ and diffusion/dispersion coefficient D. The form of the flux in Equation (12) assumes diffusion coefficients to be species independent.

Mineral reaction rates I_m have the form based on transition state theory given by

$$I_m = -k_m a_m \mathcal{P}_m \left(1 - K_m Q_m\right) \zeta_m, \tag{13}$$

where for the mth mineral, k_m denotes the kinetic rate constant, a_m represents the specific surface area, P_m denotes a prefactor to account for the dependence of the rate on pH and other species, K_m denotes the equilibrium constant, and Q_m the ion activity product defined by

$$Q_m = \prod_j (\gamma_j C_j)^{\nu_{jm}^{\mathrm{min}}}. \tag{14}$$

The factor ζ_m takes on the values zero or one to ensure that if a mineral is not present at some m particular point in space, it cannot dissolve:

$$\zeta_m = \begin{cases} 1, & \varphi_m > 0 \ \text{ or } \ K_m Q_m > 1, \\ 0, & \varphi_m = 0 \ \text{ and } \ K_m Q_m \le 1 \end{cases}. \tag{15}$$

The mineral mass transfer equation has the simple form

$$\frac{\partial \varphi_m}{\partial t} = \overline{V}_m I_m, \tag{16}$$

where $\bar{V}_m$ and φ_m refer to the molar volume and volume fraction, respectively, of the *m*th mineral.

4. Hanford 300 Area Conceptual Model

4.1. Spatial Discretization

The Hanford 300 Area model considers a three-dimensional problem domain measuring 900 × 1300 × 20 meters (*x*, *y*, *z*) in size, rotated at 14° counter-clockwise about the *z*-axis at the origin for alignment with the Columbia River as illustrated with the yellow box in Figure 2. The base of the model domain lies at 90 meters elevation above sea level. The discretized grid is composed of 1,872,000 uniformly-spaced grid cells with 5-meter horizontal and 0.5-meter vertical grid spacing.

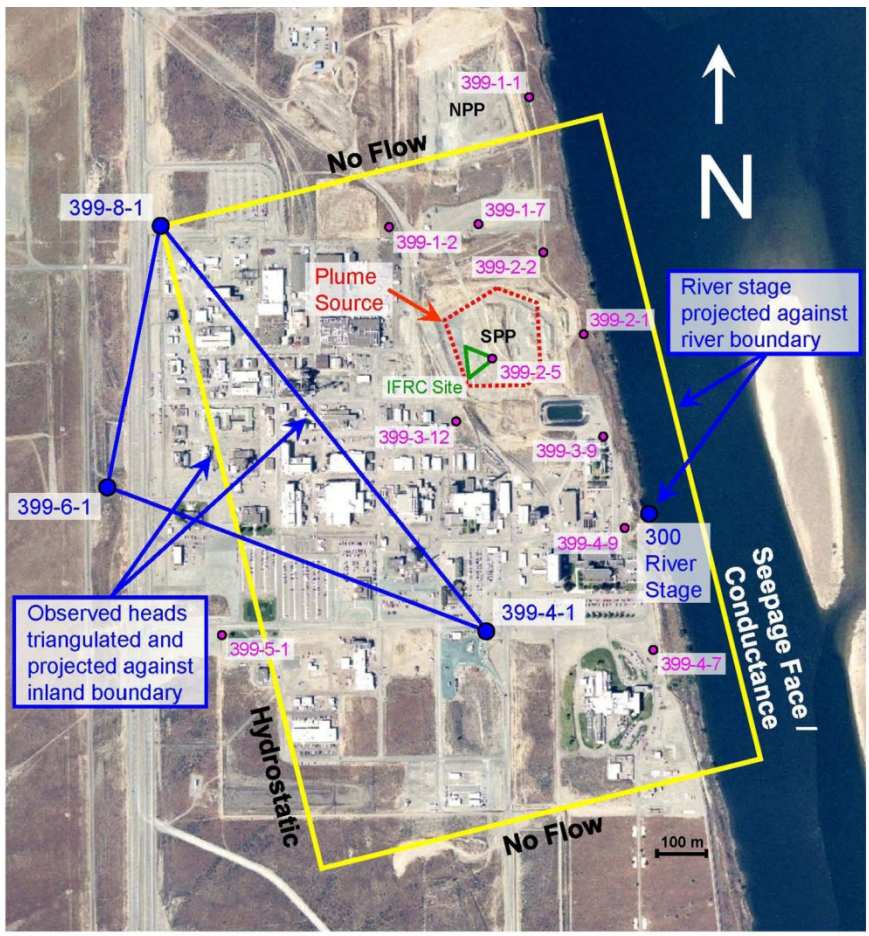

Figure 2. Planar view of outline of 3D computational domain (yellow line) showing the locations of the North and South Process Ponds (NPP & SPP), the IFRC field site, and a subset of observation wells. The transient inland boundary condition at the western edge is constructed by projecting head data obtained from wells 399-8-1, 399-6-1 and 399-4-1 onto the western boundary. The transient Columbia River stage is projected onto the river boundary to the east. No flow boundary conditions are imposed on the north and south faces.

4.2. Hydrogeology

The geologic conceptual model for the Hanford 300 Area is based on a three-dimensional solids model of the site constructed by delineating the ground surface, river bathymetry, and underlying hydrostratigraphic units. For this modeling effort, three geologic units are considered: (1) Hanford sands and gravels, (2) Ringold fine-grained silts, and (3) Ringold gravels. The Hanford unit extends from the surface of the site through the vadose zone to below the water table with the contact between the Hanford and Ringold units forming an undulating surface, as viewed from the southeast in Figure 3. Hydraulic properties for these units (i.e., porosity φ, tortuosity τ, van Genuchten parameters α and m, residual saturation S_r, and permeability k) were obtained from [9]. The permeability of the upper Hanford unit, which governs the rate at which fluid flows through it, is two to three orders of magnitude larger than that of the lower Ringold units. Therefore, most groundwater flow to the river is through the Hanford unit in the upper portion of the model domain.

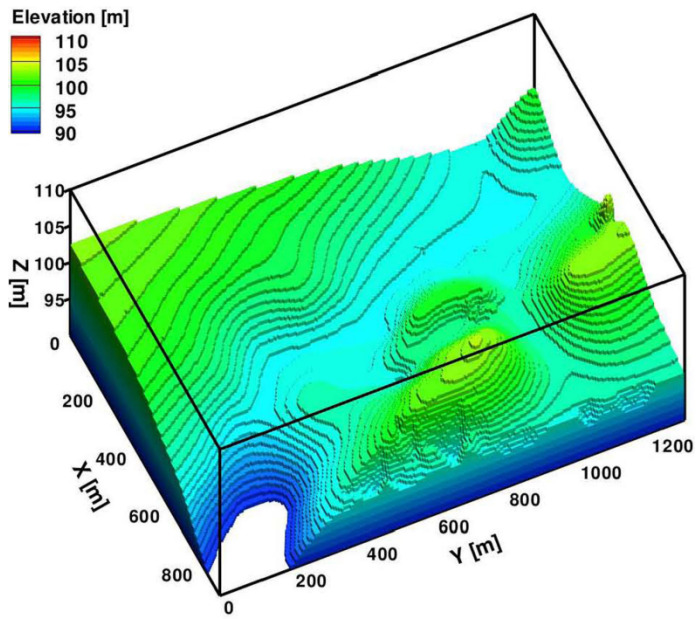

Figure 3. Hanford-Ringold contact with elevation contoured on the Ringold units and the upper Hanford unit hidden.

Material properties are specified within the computational domain by superimposing the PFLOTRAN grid on the 3D solids model and assigning material IDs to cells based on their location within the solids model. Grid cells above the ground surface and river bottom are considered inactive, while active cells are assigned material properties based on cell material IDs. Permeabilities for stochastic simulations incorporating heterogeneity are assigned only to the Hanford unit since the lower Ringold units could be considered relatively impermeable, though they clearly are not.

4.3. Geochemistry

The geochemical conceptual model consists of 15 primary aqueous species (H^+, Ca^{2+}, Cu^{2+}, Mg^{2+}, UO_2^{2+}, K^+, Na^+, HCO_3^-, Cl^-, F^-, HPO_4^{2-}, NO_3^-, SO_4^{2-} and two tracers), 88 secondary 2 3 434 aqueous complexes, two kinetically-reacting minerals (Calcite and Metatorbernite), two surface complexes (>$SOUO_2OH$ and >$SOHUO_2CO_3$) and one surface site (>SOH). Important geochemical reactions for equilibrium surface complexation and mineral dissolution include:

$$>\mathrm{SOH} + \mathrm{UO_2^{2+}} - 2\ \mathrm{H^+} + \mathrm{H_2O} \rightleftharpoons >\mathrm{SOUO_2OH}, \tag{17a}$$

$$>\mathrm{SOH} + \mathrm{UO_2^{2+}} - 2\ \mathrm{H^+} + \mathrm{H_2O} + \mathrm{CO_2} \rightleftharpoons >\mathrm{SOHUO_2CO_3}, \tag{17b}$$

$$2\ \mathrm{UO_2^{2+}} + \mathrm{Cu^{2+}} + 2\ \mathrm{HPO_4^{2-}} + 8\ \mathrm{H_2O} - 2\ \mathrm{H^+} \rightleftharpoons \mathrm{Metatorbernite(s)}, \tag{17c}$$

$$\mathrm{Ca^{2+}} + \mathrm{CO_2} - 2\ \mathrm{H^+} + \mathrm{H_2O} \rightleftharpoons \mathrm{Calcite(s)}. \tag{17d}$$

Selectivity coefficients for the two surface complexes are taken from [10]. Mobility of uranium is also a affected by aqueous complexation reactions with the two dominant species being $\mathrm{CaUO_2(CO_3)_3^{2-}}$ and $\mathrm{Ca_2UO_2(CO_3)_{3(aq)}}$. Overall, 28,080,000 geochemical degrees of freedom are represented in the model. Further details regarding the geochemistry (e.g., initial and boundary concentrations, dominant aqueous U(VI) species, etc.) may be found in [8].

4.4. Boundary and Initial Conditions

The western boundary condition for the model is a transient hydrostatic condition with pressures calculated through the triangulation and interpolation of inland well head data and projection along the western face. The eastern river boundary is a dynamic seepage face/conductance condition (above and below river stage, respectively) that mimics the influence of the river bank and river bottom sediment on river-groundwater interaction. The transient eastern boundary pressures are calculated from river stage and river gradient data. No flow boundary conditions are assigned to the north and south boundaries of the model, while recharge due to precipitation is modeled through a specified flux at the top surface.

The model initial condition is set by running a simulation without sorption for several years where the U(VI) plume emanates from the source zone in the foot print of the South Process Pond (see Figure 2) and is transported toward the river. After several years, this plume reaches a quasi steady state and does not grow significantly in size. At this point, the simulation is checkpointed, and upon restart the sorbed U(VI) concentrations are equilibrated with the aqueous phase geochemistry. The model then proceeds through the year-long simulation with sorption incorporated in the geochemistry. This “restart” approach allows the model to bypass the U(VI) plume emplacement phase in time, the which is highly uncertain with regard to the magnitude and time of release.

5. Simulation Results

As discussed in Section 2, numerical simulation can be employed in an attempt to predict the flux of U(VI) from the Hanford 300 Area to the Columbia River. PFLOTRAN simulations were run based on the conceptual model described in Section 4 to estimate this flux. Both homogeneous and heterogeneous permeability fields were considered in these simulations. For the homogeneous simulations, 4096 processor cores were employed for ~5 hours on Oak Ridge National Laboratory’s Jaguar XT4/5 supercomputer to complete a 1-year simulation. In the case of the stochastic simulations with ten heterogeneous permeability fields, PFLOTRAN’s multi-realization capability was utilized to run all ten simulations simultaneously on 40,960 processor cores, each simulation employing 4096 cores. These stochastic simulations required an increased 10–11 hours to complete (as opposed to the ~5 hours for the homogeneous runs), primarily due to an increased number of linear solver iterations in the flow solve, likely a result of incorporating heterogeneity. Altogether, the ten stochastic simulations consumed ~450K cores hours on Jaguar. Assuming a conservative 50% parallel efficiency for PFLOTRAN, these simulations would have required ~25 years to run on a single desktop computer, assuming the sufficient memory were available.

Figure 4 illustrates the cumulative U(VI) flux to the Columbia River of ~25 kg/yr for a homogeneous Hanford unit permeability field. This 25 kg/yr result is in close agreement with estimates of 20–50 kg/yr predicted by field hydrologists at the site (Peterson, pers. comm.). Figure 4 depicts river stage in the background with cumulative U(VI) flux observed for the cases of no sorption, equilibrium sorption, and multirate kinetic sorption, where sorption and surface

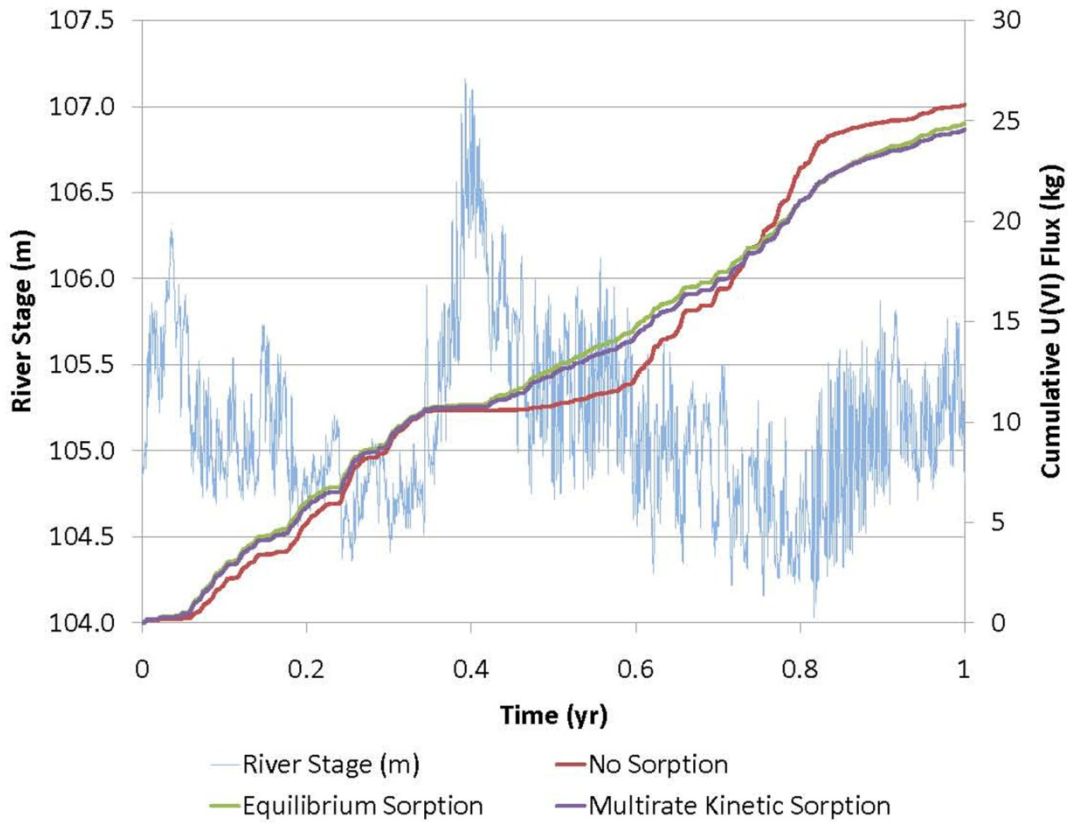

Figure 4. Cumulative flux for equilibrium and multirate sorption, and no sorption, at the river-aquifer boundary plotted as a function of time.

complexation are synonymous. From the plot it is evident that there is little difference between the equilibrium and multirate kinetic surface complexation formulations for U(VI) sorption. This result is likely true only for a conceptual model that assumes that the plume spans the distance from the source zone to the river without the source becoming depleted. One would expect the flux based on equilibrium surface complexation to be higher once the non-labile U(VI) in the source zone ceases to exist.

The cumulative U(VI) flux for the non-sorbing case is similar to that of both sorption cases. This result is non-intuitive but can be explained. For both the equilibrium and multirate kinetic surface complexation scenarios, the number of sorption sites that are "occupiable" are occupied from the beginning of the simulation (recall that the sorbed U(VI) is equilibrated with the aqueous geochemistry for an initial condition). Thus, there are few to no occupiable sites available for surface complexation as the simulation proceeds and the U(VI) is transported to the river in an essentially unretarded manner. Clearly, the non-sorbing and sorbing results are not identical, particularly when river water seeps far inland from 0.35–0.55 years time pushing the U(VI) plume to the west for the non-sorbing case. However, it is evident that both surface complexation scenarios exhibit a nearly-linear mass rate or flux to the river of similar magnitude to the non-sorbing case, which suggests the lack of occupiable sorption sites.

To illustrate the impact of heterogeneous permeability on the U(VI) flux to the river, ten stochastically-generated heterogeneous permeability fields were incorporated within the conceptual model. The parameters and procedure employed to generated these random data sets are described in detail by [11]. Figure 5 illustrates a representative realization of one of these heterogeneous fields.

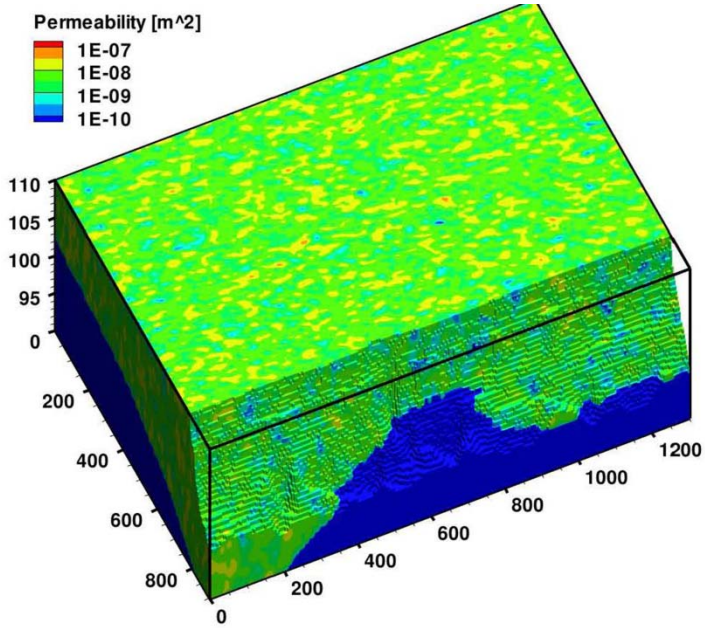

Figure 5. Heterogenous k_{xx} field for stochastic simulation. *Z*-magnification = 32×.

Figure 6 shows the variability in the cumulative U(VI) flux for the ten realizations of heterogeneous permeability, where all ten cumulative fluxes at one year are within 7% of each other. This result demonstrates a low sensitivity of the U(VI) flux to the heterogeneous permeability fields employed within the model. It should be noted that these heterogenous fields were generated based on data sets provide by the Hanford 300 Area Integrated Field Research Challenge (IFRC) project, which occupies a plot-scale region much smaller than the plume-scale conceptual model presented in this work. It is uncertain whether the plot-scale IFRC data sets can be accurately extrapolated to the plume scale. [11] provides a detailed analysis of the strengths and weaknesses of this stochastic groundwater study and discusses the potential need for incorporating larger-scale heterogeneities within the plume-scale conceptual model to better quantify uncertainty.

6. Conclusion

In this work, the reactive multiphase flow and geochemical transport code PFLOTRAN was employed to simulate migration of U(VI) at the Hanford 300 Area and quantify the flux of U(VI) leaching into the neighboring Columbia River over the course of a year. Simulations run on thousands to tens of thousands of processor cores on ORNL's Jaguar supercomputer predicted that approximately 25 kilograms of U(VI) are discharged into the Columbia River each year. The simulations also demonstrated that this U(VI) flux estimate is only slightly sensitive to small-scale heterogeneity in permeability within the site's geology. Future plans for simulation at the site include the utilization of PFLOTRAN's adaptive mesh refinement capability (currently being implemented) to improve numerical accuracy near the Hanford 300 Area IFRC site.

7. Acknowledgements

This research is supported under the U.S. Department of Energy SciDAC-2 (Scientific Discovery through Advanced Computing) program with funding provided by DOE Offices of Biological & Environmental Research (BER) and Advanced Scientific Computing Research (ASCR). Supercomputing resources were provided by the DOE Office of Science Innovative and Novel Computational Impact on Theory and Experiment (INCITE) program with allocations on NCCS Jaguar at Oak Ridge National Laboratory.

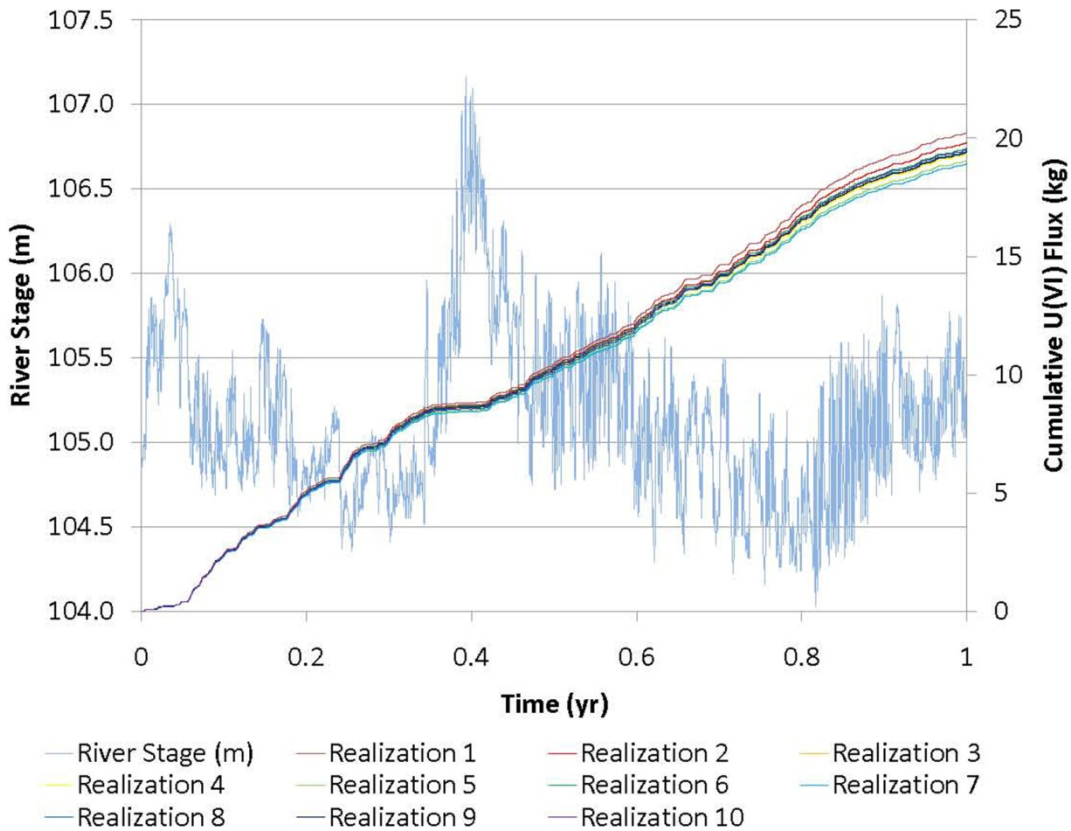

Figure 6. Comparison of cumulative U(VI) flux to Columbia River for ten realizations of permeability.

References

[1] DOE. 1994. Remedial investigation/feasibility study report for the 300-FF-5 Operable Unit, Report DOE/RL94-85, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

[2] ROD. 1996. Declaration of the Record of Decision, U.S. DOE Hanford 300 Area-FF-1 and Hanford-FF-5 Operable Units, Hanford Site, Benton County, Washington Tech. rep., Washington State Department of Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy, Richland, Washington.

[3] Zachara J M, Davis J A, Liu C, McKinley J P, Qafoku N, Wellman D M, and Yabusaki S. 2005. Uranium geochemistry in vadose zone and aquifer sediments from the 300 Area uranium plume, Report PNNL-15121, Pacific Northwest National Laboratory, Richland, Washington.

[4] Hammond G E, Lichtner P C, Mills R T, and Lu C. accepted *Ground Water Reactive Transport Models*. chap PFLOTRAN: Reactive Flow & Transport Code for Use on Laptops to Leadership-Class Supercomputers.

[5] Richards L A. 1931. *Physics* **1** 318–333.

[6] van Genuchten M T. 1980. *Soil Science Society of America Journal* **44** 892–898.

[7] Burdine N. 1953. *Transactions of the American Institute of Mining and Metallurgical Engineers* **198** 71–78.

[8] Hammond G E and Lichtner P C. accepted *Water Resources Research*.

[9] Williams M D, Rockhold M L, Thorne P D, and Chen Y. 2008. Three-dimensional groundwater models of the 300 Area at the Hanford Site, Washington State Report PNNL-17708 Pacific Northwest National Laboratory, Richland, Washington.

[10] Bond D L, Davis J A, and Zachara J M. 2008. *Adsorption of Metals by Geomedia II: Variables, mechanisms, and model applications* 375–416.
[11] Hammond G E, Lichtner P C, and Rockhold M L. 2010. *Journal of Contaminant Hydrology* doi:10.1016/j.jconhyd.2010.04.005.