

Representation of Rate-Limited Sorption in Model Simulation of Pump-and-Treat Remediation at the Fernald, Ohio DOE Site

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ABSTRACT

A groundwater flow and reactive transport model (MODFLOW and RT3D) was calibrated to an extensive data set from over a 15 year period in order to evaluate the cleanup timeframe of uranium-contaminated groundwater at the former Feed Materials Production Center located in Fernald, Ohio. Previous transport modeling, which assumed equilibrium between dissolved and sorbed phases, has consistently under-predicted the time to reach MCLs. The model in this study assumed rate-limited sorption in order to represent the disequilibrium between sorbed and dissolved phases that can occur particularly near recovery wells where groundwater velocities are higher. This representation of rate-limited sorption provided a better match of the slower cleanup rates observed in monitor wells at the site. As a result of the extensive data set available at Fernald (e.g., monthly extracted mass from pumping, transient concentration data from over 100 wells, sorbed-phase speciation), the Fernald site provides an opportunity for more accurate simulation of the net effect of sorption/desorption on dissolved phase concentrations. The calibrated model in this study indicated slower desorption rates and predicted a significantly longer time to reach cleanup standards relative to previous modeling. Recent concentration data from ongoing monitoring at the site supports these slower cleanup rates and a longer cleanup timeframe.

INTRODUCTION

Pump-and-treat (P&T) remediation is often the only viable remedial technology for many sites with large groundwater contaminant plumes. The attainment of reasonable estimates of the time required for a P&T system to achieve cleanup is often difficult for some contaminants because of the interaction of the dissolved plume with the aquifer grains through adsorptive and desorptive processes. If these processes are rapid with respect to groundwater flow, the dissolved and sorbed phases are in equilibrium and can be approximated using a distribution coefficient (K_d). If these processes are slow with respect to groundwater flow, the relationship is in non-equilibrium (rate-limited). The equilibrium approach for simulating interaction between the sorbed and dissolved phases is typically inaccurate under these conditions. During P&T remediation, the elevated groundwater flow velocities that are established within the plume can create rate-limited desorption conditions. Groundwater transport modeling at the US DOE site in Fernald, Ohio serves as a useful case study of how representation of rate-limited desorption can potentially achieve a more accurate transport calibration and better estimate of the clean up timeframe in comparison to models using the more conventional equilibrium (K_d) approach.

Fernald site closure, completed in 2006, included the staged installation of a P&T system to remediate a 187 acre total uranium plume (based on an MCL of 30 ug/L). P&T operations were initiated in 1993, were expanded in 1998 and 2003, and currently consist of 23 extraction wells with a combined capacity of 6.8 million gallons per day (mgd). From its inception through 2008, the system has extracted over 9,000 pounds of uranium from 23 billion gallons of groundwater (DOE, 2009).

Situated at the southernmost extent of the Pleistocene glaciation, the site is underlain by glacial till and outwash sediments deposited in a buried valley eroded into Ordovician dolomitic shale and limestone. Wisconsin age till underlies the site from ground surface to a depth of approximately 30 feet. Beneath the till are thick sand and gravel outwash deposits that extend to a maximum depth of 200 feet; the Great Miami aquifer (GMA) consists of the saturated portion of these deposits. The regional water table occurs in the GMA at depth of approximately 20 to 30 feet beneath the base of the surficial till.

During most of the period that the facility was actively processing uranium (1951-1989), uranium-contaminated water entered the GMA predominantly as storm runoff through breaches in the till created by surface water drainage features. The key drainages features include Paddys Run, which flows southward along the western border of the site, and the Storm Sewer Outfall Ditch, which originates at the site's southern boundary and is a tributary to Paddy's Run. At the outset of P&T remediation in 1993, the maximum observed total uranium concentrations ranged between 2,000 and 2,500 ug/L (DOE, 1995).

MODELING APPROACH AND RESULTS

The MODFLOW finite-difference grid covers approximately 23 square miles (Figure 1) and consists of 263 rows and 252 columns. Based on a geologic model, the model uses 13 layers to represent the saturated GMA sediments. A no-flow boundary corresponding to the bedrock surface defines the model base and lateral contact of each layer with bedrock at the valley walls. Constant head boundaries, placed normal to valley axes and located remote from the Fernald site, were used to account for groundwater flow to and from the GMA beyond the model domain. The Great Miami River, which flows near the eastern and southern boundaries of the model, was represented using constant head cells placed in the top layer. Individual segments of Paddys Run and the Storm Sewer Outfall Ditch were represented using MODFLOW's river or drain packages, depending on whether the segment was typically gaining or losing water to the GMA, respectively. Precipitation-based recharge was zoned depending on the presence or absence of till at ground surface. A relatively low rate (six inches/year) was applied to the till areas; a higher rate (15 inches/year) was used for the non-till areas.

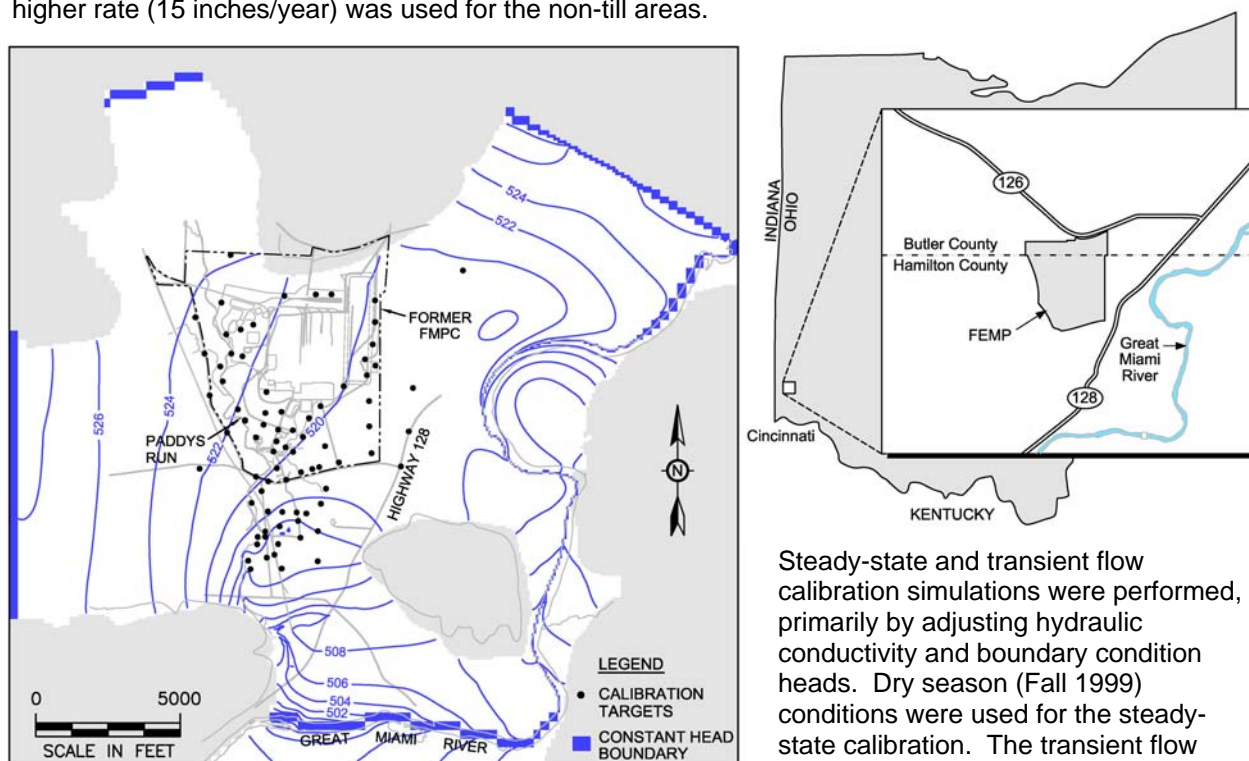


Figure 1. Map Showing Model Domain and Representative GMA Water Levels and Regional Location Map.

Steady-state and transient flow calibration simulations were performed, primarily by adjusting hydraulic conductivity and boundary condition heads. Dry season (Fall 1999) conditions were used for the steady-state calibration. The transient flow calibration period was from 1993 to 2005, corresponding to the beginning of site P&T operations and to the most recently available data at the time the calibration was performed (2005). Table 1 shows residual statistics for both calibrations.

In general, the model closely matched the groundwater levels observed in the target monitoring wells. The statistics show that the mean target residuals are close to zero and that the residual standard deviations are low in comparison to the observed ranges.

Calibration	No. Wells	Residual Mean (ft)	Residual Std. Dev. (ft)	Res. Mean (ft)	Range (ft)	Std. Dev./ Range
Steady State	79	0.02	0.6	0.4	11.1	0.05
Transient	308	0.52	3.24	2.02	100.13	0.032

Groundwater in the shallow, contaminated portion of the aquifer is a carbonate-type water and is generally oxidizing. Dissolved uranium, therefore, may occur in uranyl form

(UO_2^{+6}) and, more likely, as U^{+6} carbonate species, both of which are mobile in groundwater. Uranyl also complexes with other major anions including phosphate and hydroxide which are present or likely present in site groundwater. A sequential extraction study of aquifer material samples (Bryan et al., 2003) from the highest concentration portions of the plume revealed that approximately 25 percent of the uranium contained in the aquifer sediments is loosely bound and is readily exchangeable through ion exchange processes. In addition, the study determined that 38 – 48 percent is associated with carbonate minerals. About one third of this uranium is liable (e.g., is adsorbed and can desorb) and the remainder is mineralized (non-liable). The amount of uranium associated with amorphous and crystalline iron oxides is minor. Although the uranium precipitated with the amorphous iron oxyhydroxides appears sequestered, uranium precipitated with the crystalline oxyhydroxides is liable. Uranium contained in the aquifer grain minerals is very minor and comparable to the concentration in uncontaminated aquifer sediments.

The available aqueous and solid-phase data, although relatively extensive with regard to uranium and other contaminants of concern, was insufficient for the quantification of the above reactions within a multispecies reactive transport model. As discussed above, uranium is liable through ion exchange processes and through desorption from carbonates and, to a lesser extent, crystalline oxyhydroxides. The selected modeling approach was to adopt the rate-limited sorption approach described in Haggarty and Gorelick (1994) in which a first-order reaction rate parameter is used to represent all relevant processes collectively. To implement this approach, the Rate-Limited Sorption Reactions Option in the RT3D groundwater transport model was selected for transport. In accordance with this approach, RT3D simulated concentration changes in both the sorbed and the dissolved phases.

With flow based on the 1993 – 2005 transient model, the solute transport model was calibrated using uranium concentrations measured in 122 site monitoring wells. Data from up to 32 monitoring events (quarterly then semi-annual frequency) were available for most wells through this period. Known active contamination source areas were included in the model until the respective time when remediation of each of these sources was completed.

The transport parameters adjusted during calibration included the first-order reaction rate coefficient, K_d , dispersivity, and starting concentrations for both the dissolved and sorbed phases. Dissolved phase concentrations were obtained by kriging 1993 concentration data with some follow up adjustment in portions of the grid away from measured values. Starting concentrations for the sorbed phase were specified by multiplying the aqueous phase concentrations by a constant based on field data. Final transport values are summarized below.

Parameter	Reaction Parameter (day^{-1})	Distribution Coefficient (mL/g)	Sorbed Conc. Factor (dimensionless)	Dispersivity (ft)
Range	0.005 - 0.06	0.1 - 7.3	13.5 - 0.5	100 - 25
Final Value	0.03	4.0	5.3	25

In addition to site monitoring well concentration histories, other measured site parameter data were

matched during the calibration. This includes the extracted mass from the P&T system and available liable uranium concentration data measured from the GMA aquifer matrix. In general, the transport model reasonably matched dissolved phase concentrations (see table below) and closely approximated the measured extracted mass. For the sorbed phase, however, the model results were biased lower, ranging from three to 73 percent of the associated measured value.

Component	Units	Data Pts.	Residual Mean	Residual Std. Dev.	Res. Mean	Range	Std. Dev./ Range (Dimensionless)
Dissolved	ug/L	122	-1.93	40.8	16.6	845	0.05
Sorbed	mg/kg	12	644	605	771	1311	0.46

Improvements to the sorbed match resulted in a corresponding degradation of the dissolved phase match. However,

given the scarcity of measured sorbed phase concentrations, the location bias of these measurements to the most contaminated portions of the plume, and the resulting uncertainty regarding representativeness, a greater weight in the transport calibration was given to accurately matching the dissolved phase.

To evaluate the effectiveness of the rate-limited approach versus the equilibrium approach, the model was re-run with the equilibrium approach in order to simulate sorption/desorption. For this model, a uniform K_d of 4.0 mL/g was specified for the entire model. A comparison of simulation results with the rate-limited approach shows that the rate-limited approach more accurately matches observed conditions.

Figure 2 compares the measured 2009 plume (defined using the 30 ug/L isopleth) with the predicted plumes from the two simulation approaches. The rate-limited predicted plume more closely approximates the observed plume. Figure 3 compares the observed concentration history in Monitoring Well 2095 with simulated concentrations for both approaches for both the calibration period and 25 year predictive period. The rate-limited concentrations match reasonably well with the measured concentrations for this well while the equilibrium concentrations generally underestimate the measured values. To compare the overall performance from calibration through prediction, cumulative desorbed mass for each model is compared to extracted mass (Figure 4). The desorbed mass is consistently greater for the rate-limited sorption model compared to the equilibrium sorption model. The greater dissolved mass for the rate-limited approach corresponds to higher concentrations through the calibration phase, which is consistent with both the observed data and more realistic predicted cleanup timeframe. Previous models using the equilibrium-approach predicted that cleanup of the GMA would be achieved by 2023 (DOE, 2004) as compared to 2042 for the rate-limited approach.

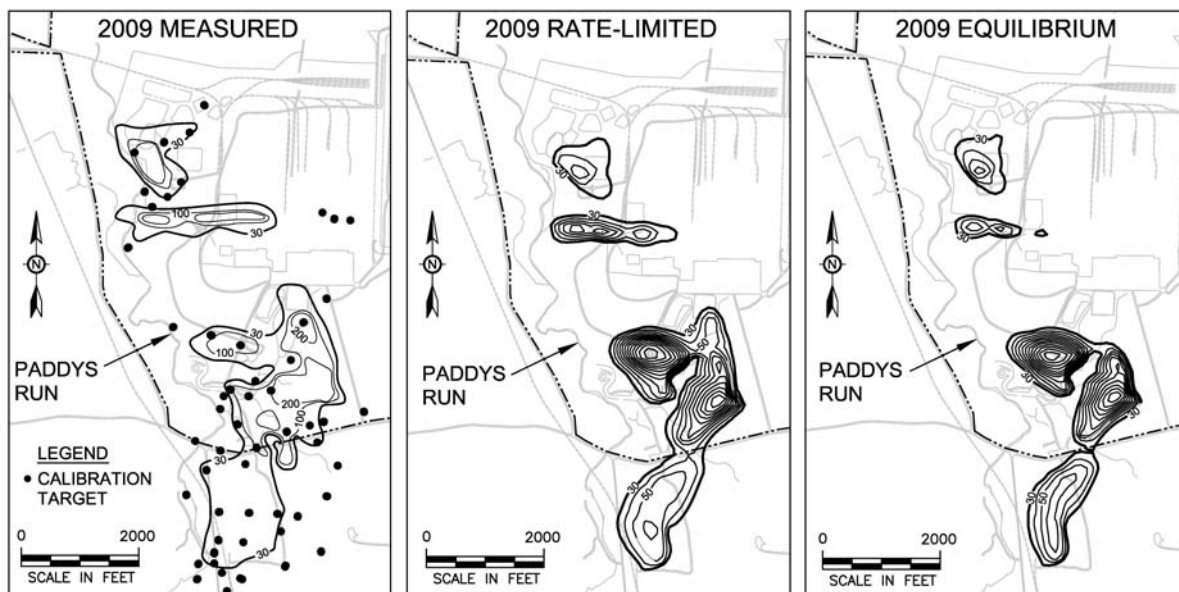
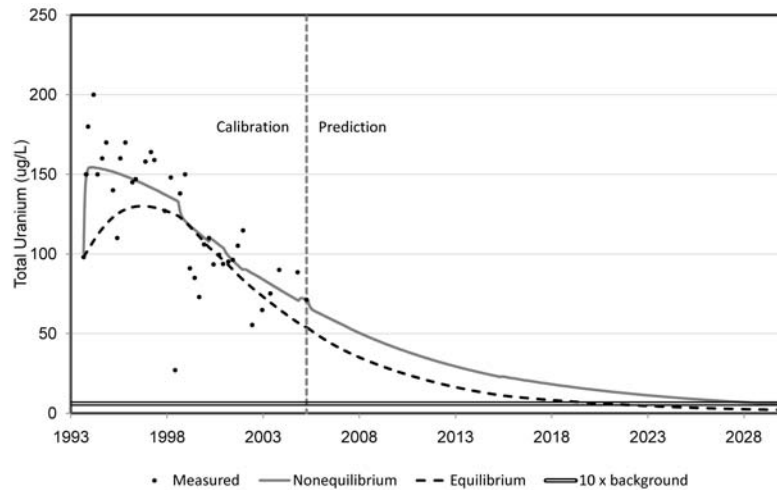


Figure 2. Comparison of Measured, Rate-Limited, and Equilibrium Plumes (2009).

Simulation of groundwater cleanup at the Fernald DOE site provides an example application of the rate-limited sorption/desorption approach in transport modeling. The application of this approach and the comprehensive data set compiled by DOE in evaluating remedy progress enabled a fairly accurate



transport calibration to be achieved and a more realistic prediction of the time required for completing the groundwater remediation.

Figure 3. Comparison of Measured Rate-Limited and Equilibrium Simulated Concentrations at a Selected Monitoring Well.

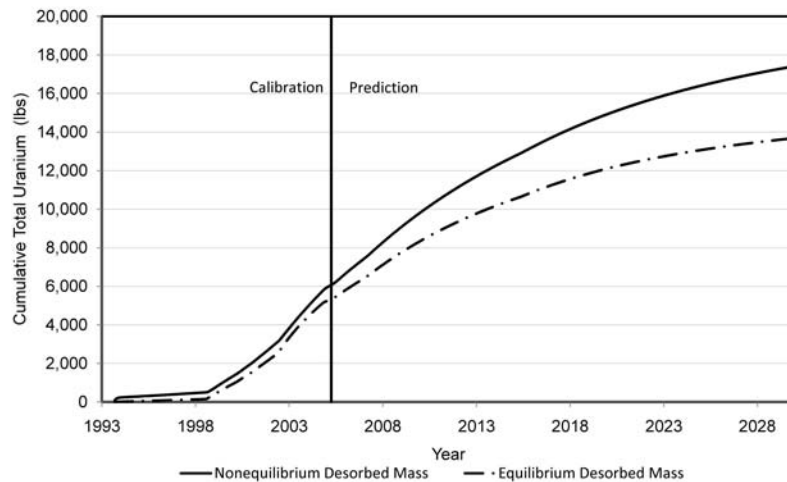


Figure 4. Comparison of Desorbed Mass for the Rate-Limited and Equilibrium Simulations.

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