Modeling of Uranium Sorption/Desorption with Advection

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Objectives

- Evaluate conceptual and mathematical models to describe slow sorption and desorption/dissolution reactions in 300A contaminated vadose zone sediments.
- Apply the models to saturated and unsaturated transport data where strong kinetic effects were observed.
- Test appropriate kinetic rate formulation for field scale application.

A Distributed Kinetic Sorption and Desorption/Dissolution Model

U sorption and desorption/dissolution was assumed to occur on multiple sites with different chemical kinetic or diffusive mass transfer rates, and reaction constants:

$$\frac{\partial S}{\partial t} = \sum_{i=1}^{N} \frac{\partial S_i}{\partial t}; \quad \frac{\partial S_i}{\partial t} = \alpha_{\mathrm{i}} \left[f_i(\alpha_i) K_d^i C - S_i \right]$$

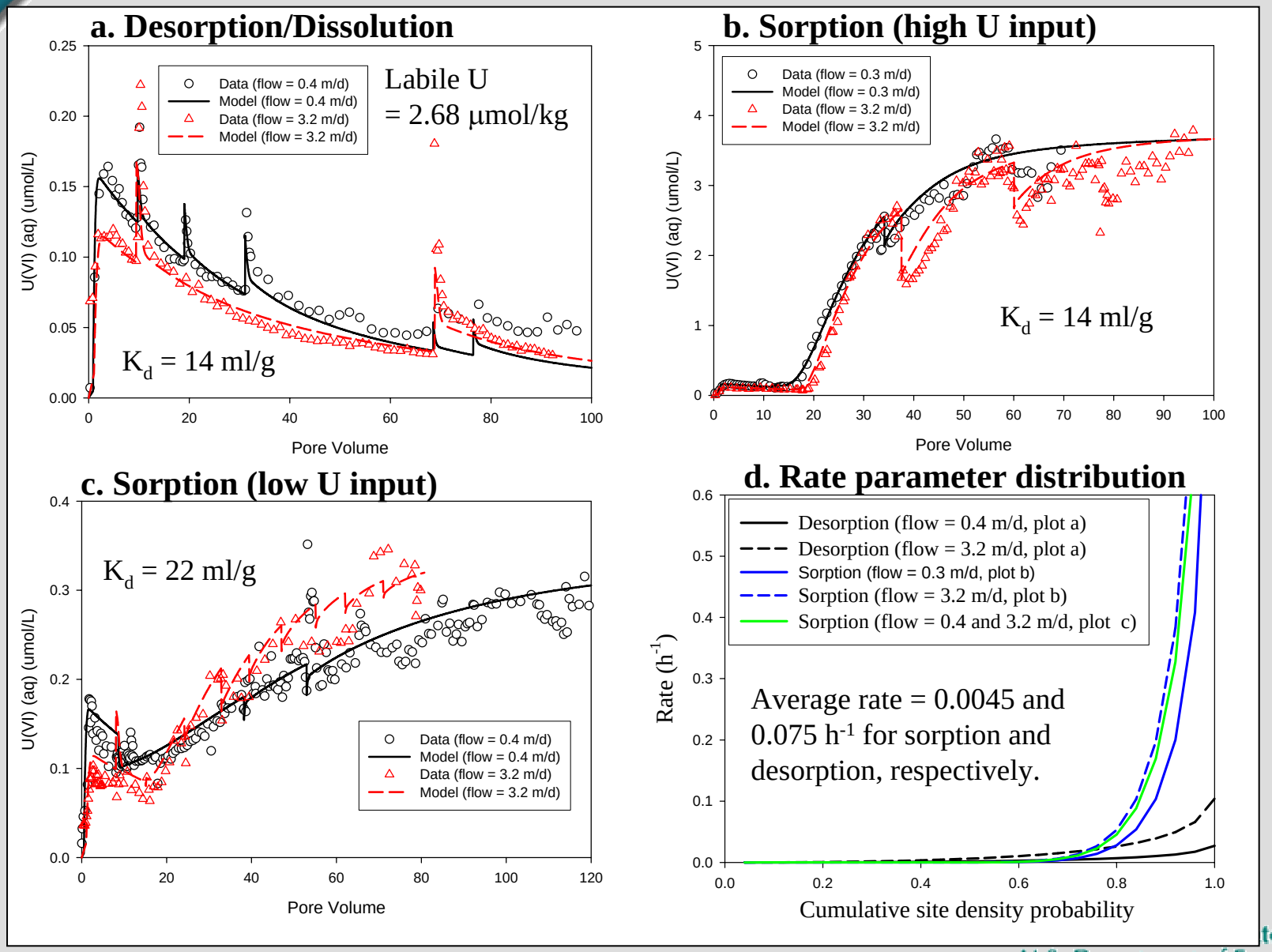
Distributed rate parameters were assumed to follow the Gamma statistical distribution (two parameters):

$$f_i(\alpha_i) = \int_{\alpha_i}^{\alpha_i + \Delta\alpha_i} \frac{\beta^{-\eta} \tau^{\eta-1}}{\Gamma(\eta)} \exp\left(-\frac{\tau}{\beta} \right) d\tau$$

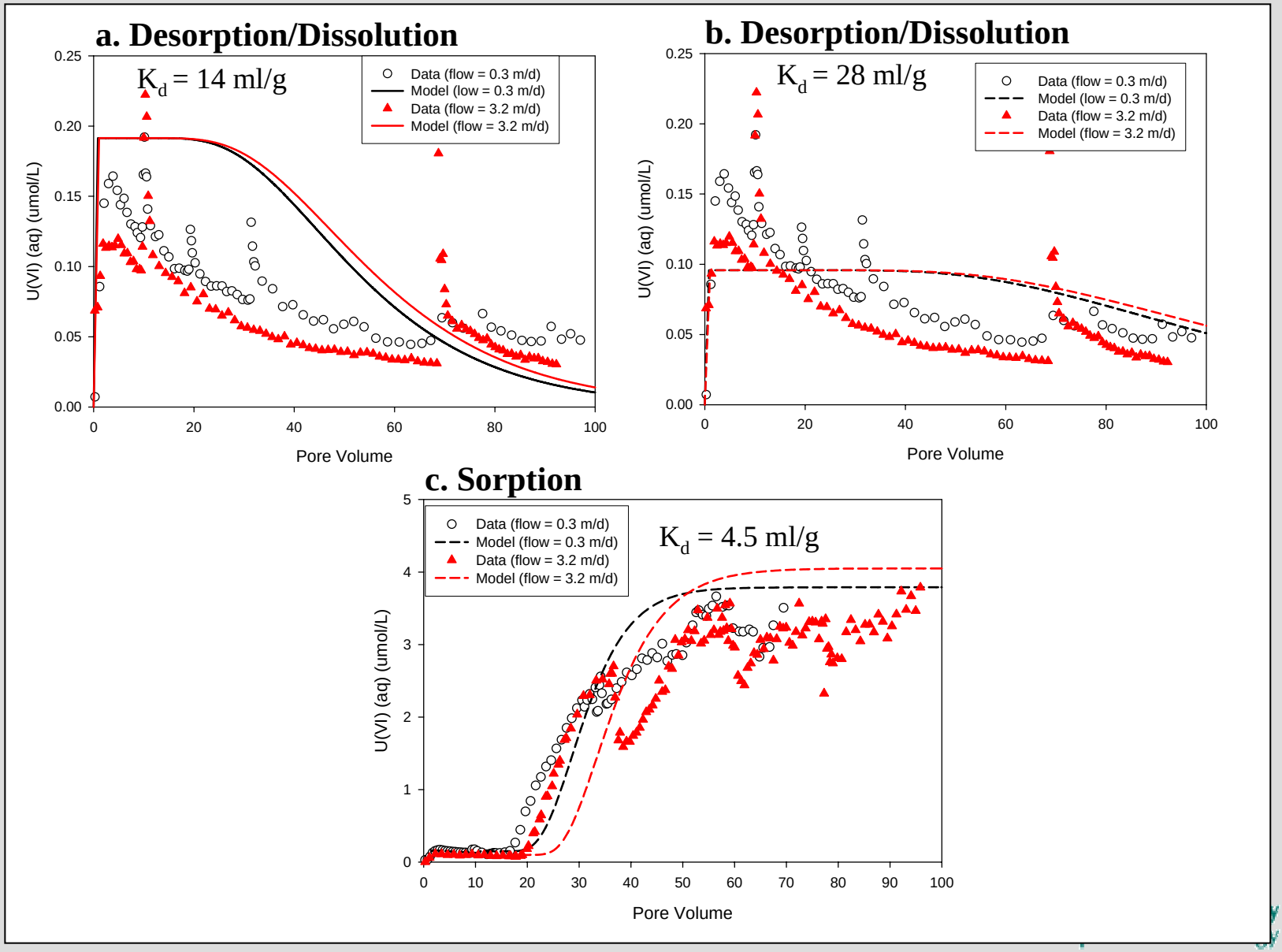
The distributed kinetic model was integrated into the advection-dispersion equation:

$$\theta \frac{\partial C}{\partial t} + \rho_b \frac{\partial S}{\partial t} = \theta D \frac{\partial^2 C}{\partial x^2} - \theta v \frac{\partial C}{\partial x}$$

Results from the Distributed Kinetic Model



Results from Equilibrium Model



Summary

- The distributed model was able to describe the kinetic sorption and desorption/dissolution results.
- Variable rates were required to describe the sorption and desorption/dissolution. The average rate of desorption/dissolution from the contaminated sediments was slower than sorption of spiked U(VI).
- The fitted sorption K_d values were a nonlinear function and were higher at lower concentration.
- U(VI) concentrations in 300A groundwater are probably kinetically controlled and a kinetic model is needed to simulate plume dynamics.

Future Modeling Work

- Using a chemical reaction constant (K_{sc}, K_{sp}) to replace K_d in the kinetic rate formulation;
- Evaluating whether the reaction constant (K_{sc}, K_{sp}) has to be treated as a distributed parameter and its correlation with kinetic rate parameters;
- Developing a mathematical model that is consistent with the measured sorption and desorption/dissolution mechanisms and macroscopic experimental results under variable chemical and physical conditions.