



# Uncertainty analysis of multi-rate kinetics of uranium desorption from sediments



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## ABSTRACT

Multi-rate surface complexation models have been proposed to describe the kinetics of uranyl (U(VI)) surface complexation reactions (SCR) rate-limited by diffusive mass transfer to and from intragranular sorption sites in subsurface sediments. In this study, a Bayesian-based, Differential Evolution Markov Chain method was used to assess the uncertainty and to identify factors controlling the uncertainties of the multi-rate SCR model. The rate constants in the multi-rate SCR were estimated with and without assumption of a specified lognormal distribution to test the lognormal assumption typically used to minimize the number of the rate constants in the multi-rate model. U(VI) desorption under variable chemical conditions from a contaminated sediment at US Hanford 300 Area, Washington was used as an example. The results indicated that the estimated rate constants without a specified lognormal assumption approximately followed a lognormal distribution, indicating that the lognormal is an effective assumption for the rate constants in the multi-rate SCR model. However, those rate constants with their corresponding half-lives longer than the experimental durations for model characterization had larger uncertainties and could not be reliably estimated. The uncertainty analysis revealed that the time-scale of the experiments for calibrating the multi-rate SCR model, the assumption for the rate constant distribution, the geochemical conditions involved in predicting U(VI) desorption, and equilibrium U(VI) speciation reaction constants were the major factors contributing to the extrapolation uncertainties of the multi-rate SCR model. Overall, the results from this study demonstrated that the multi-rate SCR model with a lognormal distribution of its rate constants is an effective approach for describing rate-limited U(VI) desorption; however, the model contains uncertainties, especially for those smaller rate constants, that require careful consideration for predicting U(VI) sorption and desorption.

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## 1. Introduction

The multi-rate approach has been used to describe rate-limited sorption and desorption of contaminants in subsurface sediments (e.g., Culver et al., 1997; Haggerty and Gorelick, 1995; Harvey et al., 1994). The multi-rate model has recently

been extended to describe rate-limited uranyl[U(VI)] surface complexation reactions (Liu et al., 2008, 2009). Surface complexation reactions (SCR) are important processes controlling U(VI) sorption/desorption and migration in subsurface sediments (Barnett et al., 2002; Curtis et al., 2004; Davis et al., 2004; Stoliher et al., 2011). Recent studies have found that U(VI) surface complexation occurs in intragranular and intra-aggregate pore surfaces (Hay et al., 2011; Stubbs et al., 2009). Consequently, U(VI) SCR behaved kinetically, rate-limited by mass transfer from sorption sites located in intragranular domains in sediments (Fox et al., 2012; Liu et al., 2008, 2009, 2011; Qafoku et al., 2005; Stubbs et al., 2009).

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A multi-rate SCR model was designed to capture the mass transfer limited behavior of U(VI) sorption and desorption (Liu et al., 2008, 2009). The model has been demonstrated to successfully describe laboratory results of U(VI) sorption to and desorption from sediments containing different uranyl speciation and with variable surface area, sorption site concentration, and microporosity (Liu et al., 2009; Shang et al., 2011; Stoliker et al., 2013). The approach has also been used to investigate field-scale uranyl reactive transport (Greskowiak et al., 2011; Ma et al., 2010) and is being used to assess future risks associated with contaminant migration at the US Hanford site, Washington.

One major challenge in using the multi-rate SCR model is to reliably estimate its rate constants, which can range in several orders of magnitude to account for heterogeneous mass transfer properties such as diffusion path and length, local porosity and pore connectivity in sediments. A typical approach in applying the multi-rate SCR model is to assume that the rate constants follow a certain type of probability distribution, such as lognormal or gamma function that is characterized by two parameters such as mean and variance in the lognormal case (Liu et al., 2008, 2009; Qafoku et al., 2005). The distribution can be physically based for ideal systems such as homogeneous sorption in intragranular domains in sphere, cylinder, or slab particles (Haggerty and Gorelick, 1995). However, for sediments containing mineral mixtures with variable grain size, shape, and intragranular pore network, the probability distribution is a pre-assumed hypothesis. While the approach has been widely used, the assumption of the rate constant distribution has never been independently analyzed or tested for sediments. In addition, credible application of kinetic models in process understanding, predictive simulations, and risk assessment requires quantification of model uncertainty. The uncertainties of the multi-rate model including model itself and its rate constants, as well as the effect of the rate constant distribution assumption on the model uncertainties have not been systematically analyzed, preventing the reliable extrapolation of the model for field scale application and risk analysis.

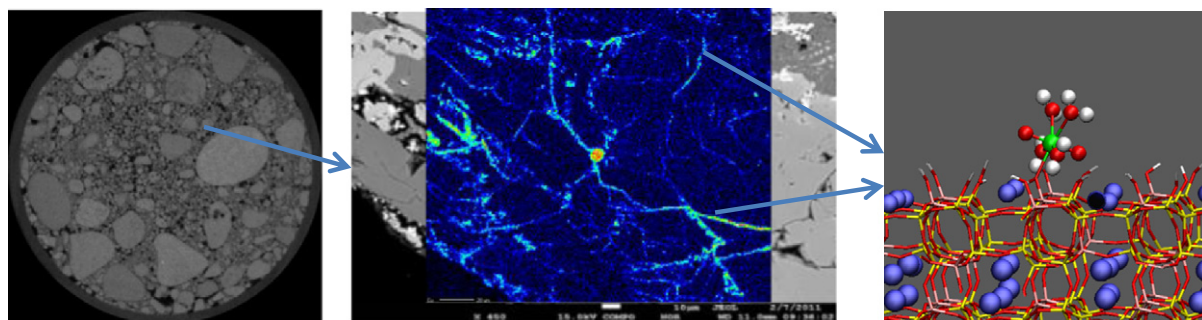
The objectives of this study are to: 1) statistically test the applicability of the lognormal assumption for the rate constants in the multi-rate SCR model, 2) estimate the uncertainty of the

multi-rate SCR model when the multi-rate SCR model is extrapolated to different geochemical conditions, and 3) identify factors controlling the model uncertainties. A Differential Evolution Markov Chain (DEMC), a Markov Chain Monte Carlo (MCMC) algorithm based on Bayesian framework, was used to estimate rate parameters and assess model uncertainty. The DEMC method was selected for its computational efficiency to estimate statistical properties for mathematical models containing a large number of parameters (Ter Braak, 2006; Vrugt et al., 2009). U(VI) desorption in stirred flow-cell reactors under variable geochemical conditions in the U(VI)-contaminated sediment from the U.S. Department of Energy (DOE) Hanford Site, Washington was used as an example for this study. The research is the first demonstration of using statistical methods to test the lognormal distribution for the rate constants in multi-rate models commonly used to describe rate-limited sorption/desorption in sediments. The paper also shows a new application of the DEMC approach, together with experimental data, to identify model uncertainty sources in characterizing and extrapolating kinetic geochemical reactions in sediments.

## 2. Models

### 2.1. Multi-rate SCR model

The multi-rate SCR model has been described elsewhere (Liu et al., 2008, 2009) and a conceptual model is provided in Fig. 1. Briefly, the model assumes that there are multiple pools of rate-limited sorption sites for surface complexation reactions in the intragranular pore domains in sediments (Hay et al., 2011; Stubbs et al., 2009). The surface complexation reactions in the intragranular domains are assumed to be fast processes that control local U(VI) sorption and desorption, while diffusive mass transfer between the intragranular domains and bulk solution is the rate-limiting step. The approach differs from other multisite approaches for metal and radionuclide sorption (e.g., Baeyens and Bradbury, 1997; Brouwer et al., 1983; Lu et al., 2012; Zachara et al., 2002) where the reaction properties such as equilibrium reaction constants are different for different sorption sites. Here the only difference between different sorption sites is



**Fig. 1.** Conceptual model of the multi-rate U(VI) surface complexation. The schematic diagram shows the heterogeneous distribution of various sediment grains (left plot), U(VI) associations in the intragranular domains (middle plot) of the sediment grains as surface complex species at the molecular level (right plot). The rate of the surface complexation is controlled by the diffusion of U(VI) species between the bulk solution and multiple intragranular sorption locations with variable local porosity, surface area, and connectivity to the bulk solution.

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