

Multiscale Modeling of Mercury Geochemistry

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In natural aquatic environments, the transport of mercury (Hg) inorganic and organic complexes takes place in flowing water and simultaneously with equilibrium and kinetic reactions. A web-based multiscale modeling aqueous speciation resource (*AQUA-MER*) has been developed for the aqueous biogeochemical speciation of metals in environment. *AQUA-MER* integrates the calculation of atomistic first-principles based thermodynamic constant with continuum-scale speciation modelling for metals. In general, the continuum-scale speciation calculations use thermodynamic stability constants ($\log K$) to predict the mesoscale distribution of Hg. However, experimental $\log K$ values are not available for many relevant complexes and for others can span ranges in excess of 10 log units. We investigated the effects of $\log K$ uncertainties on speciation calculations. We showed that thermodynamic parameter uncertainties can lead to output concentrations spanning several orders of magnitude and by performing the uncertainty analysis we could identify environmental regimes where uncertainty is important to consider in speciation modeling. Accurate and reliable quantum chemical approaches have been developed and implemented in *AQUA-MER* for the $\log K$ calculation of Hg complexation with inorganic and low-molecular weight organic compounds. High molecular weight dissolved organic matter (DOM) in the natural environment can also bind with Hg, forming stable complexes. However, the experimental $\log K$ values vary between ~ 31 and 42 log units for $\text{Hg}(\text{DOM})_2$ because of the difficulties in the molecular level characterization of the highly heterogeneous DOM. Atomistic MD simulation can capture the details of aggregation and distribution of functional groups in DOM at the molecular level. 100 ns time scale molecular dynamics simulations reveal the initial aggregation of various components of DOM forming complex structures. At the continuum-scale, a travel-time based reactive transport model in the hyporheic zone of stream corridors was established for the multicomponent Hg-DOM-S system and implemented through PFLOTRAN. Sulfur redox zonation was accounted for using a prescribed oxygen gradient. Temporal and spatial distributions of Hg-containing species along the vertical axis of a single sediment bedform were obtained and analyzed. Future studies will focus on integrating the Hg-DOM complexation mechanisms obtained from atomistic MD simulations into continuum-scale reactive transport simulations. We present an information-theoretic approach that allows for seamless integration of multi-resolution data into multi-scale simulations to upscale/downscale hydraulic conductivity of heterogeneous porous formations. Available data (at either the fine- or the coarse-scale) are used to inform models at the opposite scale by setting a probabilistic equivalence between the fine and the coarse scale, with closures (parameters and/or constitutive laws) that are learnt via minimization of observables error and mutual information across scales. We investigate how this can guide us to formulate scaling laws and we explore means to accelerate scaling of dynamic processes and to reduce data requirements.