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From Atomic Scale to Macroscopic Modeling: A Multi-Scale Framework for Mercury Biogeochemistry

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Predicting the environmental fate and transport of mercury (Hg) in terrestrial surface and subsurface systems requires a thorough and accurate description of its speciation. Continuum-scale geochemical modeling typically employs experimentally determined thermodynamic binding constants (e.g., "log K") to model the transport and transformations of metals in the environment. However, the application of this method to Hg biogeochemistry is often limited due to the lack of reliable thermodynamic data. For example, the experimentally measured log K values for Hg complexation with highly variable natural organic matter (NOM) span a considerable range of >35 log units. Furthermore, even within a single well-defined system, such as $Hg(Cys)_2$, literature values vary by >20 log units. To this end, we have generated an aqueous speciation database for Hg complexes by combining high-quality experimental data adherent to IUPAC standards with theoretical data calculated with density functional theory (DFT). Currently, the database includes over 500 experimental records for 152 inorganic and organic compounds, and continues to expand. We extend our previous work in applying DFT to predict the thermodynamic constants of Hg complexes uncertain or otherwise not available in the literature and integrate the results of 86 reactions calculated using 12 different DFT methods into the database. Further refinement of this database will provide a data resource for predicting speciation of Hg and other molecular species as well, and will therefore enable the application of the continuum-scale modeling to study Hg biogeochemistry. Future studies will focus on calibrating and improving the accuracy of the current DFT prediction model, and on linking the atomistic models to the macroscopic continuum-scale modeling framework to predict the transport and transformation of Hg in the environment.