Slow and incomplete exchange during competitive Hg(II) binding to model ligands, NOM and goethite

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The behavior of mercury (Hg) in terrestrial and aquatic ecosystems is strongly governed by interactions with organic ligands and mineral surfaces controlling its mobility and bioavailability. Speciation models based on thermodynamic stability constants assuming fast exchange between different ligand complexes are used to predict the fate of Hg in natural systems. The affinity of different ligands for Hg(II) binding is relatively well known, with reduced sulfur ligands usually outcompeting other functional groups and dominating Hg(II) speciation under many conditions. However, the exchange kinetics of Hg(II) between different ligands and the extent of irreversible binding are much less well understood.

Here, we present lab experiments studying the exchange between various Hg(II) ligands. After pre-equilibrating Hg(II) solutions for 4 days with solid-phase (carboxyl-resin, thiol-resin, goethite) and dissolved (cysteine, EDTA, Suwannee River NOM) ligands, we replaced the supernatant with a ^{198}Hg-enriched solution containing the same ligand. We then followed the change of concentrations and isotope ratios in solution over time using cold vapor quadrupole ICP-MS.

The exchange between Hg(II) bound to carboxyl-resin and dissolved Hg(II) was relatively fast and complete after 4 days. In contrast, Hg(II) bound to thiol-resin and goethite exchanged much slower and equilibrated only partially after 30 days, pointing to the formation of a non-exchangeable Hg(II) pool. Competing ligands in solution further slowed down the exchange kinetics. Hg(II)-cysteine complexes reached equilibrium with the carboxyl-resin only after 16 days and exchange of Hg(II)-EDTA was even slower. Suwannee River NOM-bound Hg(II) exhibited the lowest extent of exchange, with the size of the non-exchangeable pool corresponding to the amount of thiol groups present.

Our results revealing slow exchange and the presence of non-exchangeable Hg(II) pools illustrate the limitations of thermodynamic approaches and imply that kinetic constraints must be considered to a larger extent in the modelling of Hg(II) mobility and bioavailability in natural systems.