Overlooked Mercury Isotope Exchange Reactions in Environmental Systems

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Project Abstract: Enriched mercury (Hg) stable isotope tracers have been widely used in both laboratory and field investigations to assess biogeochemical transformations of Hg. However, previous studies rarely considered isotope exchange reactions between the newly added Hg isotope and the previously deposited Hg ("old"), as these reactions could result in redistributions of the new and "old" Hg isotopes in environmental matrices. This study examined isotope exchange kinetics of divalent Hg(II) species in various groundwater and soil matrices, including low-molecular-weight (LMW) thiols (e.g., cysteine and glutathione), dissolved organic matter (DOM), metacinnabar (β-HgS), and Hg-contaminated sediments. We found that Hg bound to LMW thiol ligands and DOM can be rapidly exchanged within minutes by the addition of another Hg isotope in a homogeneous solution. The exchange resulted in identical distributions of Hg isotopes when added at equal molar concentrations. Likewise, we observed rapid isotope exchange between newly added Hg and the mineral-associated "old" Hg(II), such as metacinnabar and a Hg(II)-contaminated sediment. However, isotope exchange did not occur between inorganic Hg(II) and methylmercury up to 2 days, likely due to the covalent bonding between Hg(II) and the methyl group. Together our results suggest potentially wide occurrences of isotope exchange reactions when an enriched Hg isotope is applied in environmental systems, and these reactions result in changes in isotopic compositions of Hg bound to organic or inorganic ligands and minerals. Therefore, interpretation of experiments using isotopically-enriched Hg without consideration of isotope exchange could lead to biased conclusions concerning Hg fate and transformation rates.