Isotope Exchange between Dissolved Elemental Hg(0), Inorganic Hg(II), and Hg(II)-bound to Organic ligands and Environmental Implications

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Mercury (Hg) isotope exchange is a common process in biogeochemical transformations of Hg in the environment, but it is unknown whether dissolved elemental $Hg(0)_{aq}$ is exchangeable with divalent Hg(II) complexed with various organic and inorganic ligands in water. Using enriched stable isotopes, we probed the rates and mechanisms of isotope exchange between $^{202}Hg(0)_{aq}$ and $^{201}Hg(II)$-bound to a suite of organic and inorganic ligands. Rapid isotope exchange (< 1 h) was observed between $^{202}Hg(0)_{aq}$ and $^{201}Hg(II)$-bound to thiol ligands, including cysteine (CYS), glutathione (GSH), and 2,3-dimercaptopropanesulfonic acid (DMPS) at the 1:1 thiol-to-Hg(II) molar ratio. The exchange resulted in two electron transfers between Hg(0) and Hg(II) with no net changes in Hg reduction or oxidation. Similarly, nearly instantaneous exchange (< 3 min) occurred between $^{202}Hg(0)_{aq}$ and $^{201}Hg(II)$-complexed with weaker ligands, such as ethylenediaminetetraacetate (EDTA) or chloride (Cl^-), at the ligand-to-Hg(II) ratio of 500 or higher. However, increase in the thiol-to-Hg(II) ratio (10:1) substantially decreased the exchange rates because of the formation of 1:2 or multiplex Hg(II):thiol complexes. Exchange reactions between $^{202}Hg(0)_{aq}$ and $^{201}Hg(II)$-bound to dissolved organic matter (DOM) followed an initial rapid, then a slow process, corresponding to exchanges of Hg(II)-bound to the low- and high-affinity binding sites on DOM. We also found that inorganic Hg(II) readily exchanged with Hg(II)-bound to thiols and DOM within minutes, and the exchange could result in equal distributions of Hg(II) isotopes bound to the ligands when isotopes were added at the same molar fractions. Together, our results demonstrate that $Hg(0)_{aq}$ is not inert but readily exchangeable with Hg(II)-ligand complexes although the exchange rates may vary greatly, depending on the binding strength of ligands and the coordination environments of Hg(II).