Mercury stable isotope exchange between dissolved Hg(0) and Hg(II)-thiol complexes

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Background: Mercury (Hg) stable isotopes have been employed to trace Hg sources and chemical transformations in the environment. In anoxic waters, dissolved Hg(0) and Hg(II)-complexes often coexist but the isotope exchange between mercury species is poorly understood. In this study, we carried out laboratory experiments to examine Hg stable isotope exchange between dissolved Hg(0)-Hg(II)–thiol complexes.

Research Methods: Experiments were performed to determine the rate at which isotopes are exchanged and isotopic equilibrium between dissolved Hg(0) and thiol-complexed Hg(II) under anoxic conditions. The dissolved Hg(0) pool was generated by a metallic Hg bead in a silicone tube, equilibrated with water. The Hg(0) in solution was then partially oxidize to form Hg(II). The Hg(0)/Hg(II) solution was reacted with either mercaptoacetic acid (MCA), mercaptopropionic acid (2-MPA), cysteine, or humic acids. The aqueous Hg(II) was allowed to complex with the thiol ligand. Once chemical equilibrium was reached, reactors were periodically sacrificed for isotopic analysis. For mass spectrometry, samples were diluted, then spiked with a calibrated 204Hg/196Hg double spike. Isotopic compositions (199Hg/198Hg, 200Hg/198Hg, 201Hg/198Hg, 202Hg/198Hg) were measured on a Nu Plasma multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS).

Results: At the beginning of the experiment, the Hg(0)/Hg(II) solution showed a δ^{202}Hg difference between the Hg(II) pool and the dissolved Hg(0) pool of 2.4‰. Addition of MCA caused Hg(II) to complex with thiol groups, and initially the Hg(II) retained its isotopic composition. Isotopic exchange between the Hg(II)-thiol complexes and the Hg(0) occurred within the first 12 hours, driving both toward isotopic equilibrium. After 48 hours, the equilibrium isotopic fractionation between Hg(0) and thiol-Hg(II) was approximately 0.7 ‰. The results suggest that Hg isotope ratios can be affected without chemical transformations taking place. In our presentation, we will discuss the implications of our findings for interpreting isotopic data collected for groundwater containing both Hg(0) and Hg(II) species.