Mercury and Mercury Isotope Fractionation during Photo-Reduction in Seawater

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PURPOSE

Mercury (Hg) is a redox-sensitive metal with complex biogeochemistry, which is unique in that it has a relatively stable gaseous form in the atmosphere allowing it to be globally distributed. Although highly toxic and bioaccumulated in aquatic food webs, many aspects of the natural cycle of Hg are not well understood or quantified, hindering our ability to model the past and present Hg cycle and future variations due to emission and climate changes. Thus, new approaches are needed to track Hg and the chemical transformations it undergoes in the environment. A rapidly growing tool is Hg stable isotope geochemistry; in particular, Hg uniquely exhibits large mass independent fractionation (MIF) of odd isotopes. It is generally thought that the signature and extent of MIF in natural samples reflects photo-reduction environment.

The ocean, one of the largest Hg reservoirs, acts as both a source and sink of Hg, with the annual flux to and from the ocean larger than the anthropogenic flux. However, the dominant factors controlling Hg deposition and loss to and from the ocean are still debated including the relative importance of photo-reduction. Currently no laboratory or controlled studies of marine Hg isotope fractionation exist, and present studies are using fractionation factors and signatures from experiments performed in water most similar to freshwater.

The purpose of this study is to explore Hg isotope fractionation during photo-chemical reduction in seawater using organic ligands similar to those found in natural systems.

METHODOLOGY

Photo-reduction experiments were performed in the lab using seawater from the Sargasso Sea (Bermuda Atlantic Time Series) and either an inorganic Hg²⁺ standard or organic monomethylmercury (MMHg) standard with the following ligands: (1) L-cysteine, (2) serine, (3) blank, and (4) blank dark control. Sub-samples of the reservoir were periodically taken to track photo-reduction over time. Light levels were held constant with visible light intensity of 248W/m², UV-A of 300W/m², and UV-B of 7W/m².

Mercury concentration of each photo-reduction time-stamp sample was measured by gas-phase atomic fluorescence spectrometry (TEKRAN®) via BrCl oxidation, SnCl₂ reduction, and dual stage gold trap amalgamation.

Photo-reduction in Seawater

Hg species in seawater are modeled to dominantly be bound to reduced sulfur organic ligands in seawater, with other weaker ligands and chloride also being significant. In our experiments, photo-reduction occurred only for Hg species bound to cysteine, a reduced organic sulfur compound, yielding a 70% reduction with a kinetic reaction rate modeled by a (pseudo-) first-order rate constant of (11±0.5) x 10⁻⁵ s⁻¹ based on a semi-log concentration change plot linear approximation with an R² value of 0.9937.

The competing reaction in these experiments is 2Cl⁻ + Hg²⁺ = HgCl₂, (K=10²⁴). When Hg was bound dominantly to chloride, as in the seawater controls, no photo-reduction was observed. While the reduced organic sulfur ligand (cysteine) resulted in photo-reduction, it is unclear whether serine, a non-sulfur organic ligand, would have displayed photo-reduction, as the chloride concentration was high enough to hinder serine – Hg complexation.

ImPLICATIONS FOR MERCURY ISOTOPE FRACTIONATION

A wide range of physical processes cause the stable isotopes of Hg to fractionate by conventional mass dependent fractionation (MDF), but only a small subset of transformations result in mass-independent fractionation (MIF). During photo-reduction of Hg species, large MIF is observed for odd isotopes only and is thought to be driven by the magnetic isotope effect, a complex phenomenon depending on several factors including hyperfine coupling, radical pair lifetime and coupling strength, spin-ordinal coupling, and diffusion factors.

The ratio of MIF for the two odd isotopes is thought to be indicative of the species undergoing photo-reduction. However, the signatures of MIF during photo-reduction have only been experimentally verified for freshwater. Thus, the aim of this study is to assess the extent and signature of MIF during photo-reduction of Hg species in seawater.

RESULTS

Figure 4: Photo-reduction experimental results, illustrating (a) Change in concentration relative to initial as a function of exposure time. Error is based on standard deviation of duplicate samples. (b) Concentration changes in logarithmic format as a function of exposure time to examine kinetics of the experiment, approximated by pseudo-first order, with an R² value of 0.9937 for cysteine.

CONCLUSIONS

Photo-reduction of mercury in seawater with a reduced organic sulfur ligand resulted in (pseudo-) first-order reaction kinetics. When Hg was bound dominantly to chloride, no photo-reduction was observed. It is unclear whether serine (a non sulfur organic ligand) would have resulted in photo-reduction, as the concentration of chloride was high enough to hinder Hg complexation by serine. Future experiments with higher serine concentration will hopefully overcome this. In comparison to other photo-reduction experiments simulated in freshwater, it is expected that Hg isotopes will display MIF during photo-reduction experiments with Hg loss.