



Fractionated mercury isotope in sediments: A quest for the processes

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Mercury is long known as an environmental contaminant that enters aquatic system as elemental Hg (0) and mostly Hg (II). During the redox reactions part of the mercury is reduced to toxic water soluble methylmercury (MeHg). Natural variations in the isotopic composition of mercury have been reported and such variations have emphasized mass dependent fractionations (MDF), while theory and laboratory experiments indicate that mass-independent isotopic fractionation (MIF) effects are likely to be found as well. This study focuses on the MIF of mercury isotopes in lake sediments and uses it as a tracer to understand mercury cycling in the natural water.

Sediment cores were collected from 4 lakes in and around Pensacola, Florida. 1 gm of wet sediment was dissolved in 5 ml of conc. aqua regia for 24 hrs, filtered through a 100 micron filter paper and mixed with ultrapure 10N NaOH solution to reduce the strength of the resulting solution to approximately 1N. Hg is measured as a gaseous phase generated by reduction of the sample with SnCl_2 in a continuous-flow cold-vapor generator connected to a Thermo-Finnigan Neptune MC-ICPMS. To minimize effects of instrumental fractionation isotope ratios were measured by sample standard bracketing and reported as δ permil relative to NIST SRM 3133 Hg standard where $\delta^A\text{Hg} = [({}^A\text{Hg}/{}^{202}\text{Hg})_{\text{sample}}/({}^A\text{Hg}/{}^{202}\text{Hg})_{\text{NIST3133}}] - 1 \times 1000$ permil. In this study we have measured the isotope ratios ${}^{198}\text{Hg}/{}^{202}\text{Hg}$, ${}^{199}\text{Hg}/{}^{202}\text{Hg}$, ${}^{200}\text{Hg}/{}^{202}\text{Hg}$, ${}^{201}\text{Hg}/{}^{202}\text{Hg}$ and ${}^{204}\text{Hg}/{}^{202}\text{Hg}$. In all the samples $\delta^{198}\text{Hg}$, $\delta^{200}\text{Hg}$, $\delta^{202}\text{Hg}$, $\delta^{204}\text{Hg}$ define a MDF sequence, where as the $\delta^{199}\text{Hg}$ and $\delta^{201}\text{Hg}$ depart from the MDF line and indicate depletion of the odd-N isotopes in sediments. The magnitude of the deviation ($\Delta^A\text{Hg}$ where A=199 or 201) as obtained by difference between the measured

$\delta^{199}\text{Hg}$ and $\delta^{201}\text{Hg}$ of the samples and the value obtained by linear scaling defined by the even-N isotopes ranges from approximately -0.1 permil to -0.5 (- indicating depletion) in sediment. The magnitude of depletion generally increases with the depth of the sediment but is not correlated with the total concentration of Hg in the sediments.

MIF of mercury isotopes have been observed before in fish, Spanish moss, coal, water (Bergquist and Blum, 2007, Ghosh et.al., 2008, Das et. al. *in prep*). Photo-reduction of Hg(II) and MeHg in water enriches the product in odd N isotopes which stays in the water column and the reduced elemental mercury is depleted in ^{199}Hg and ^{201}Hg and goes back to the atmosphere. So in general atmosphere can be considered as the reservoir for the depleted odd N isotopes and the water as the complimentary enriched reservoir. The primary species of Hg in sediments are Hg(II) and MeHg. The former is scavenged from the water column because of its high reactivity with particulates and MeHg is produced in the anaerobic sediments by sulfate reducing bacteria. The lake sediments were highly enriched in organics thus some of the Hg is associated with the organics as well. The slight depletion of the odd N isotopes in the sediments can be explained in the following ways. 1. the sediments are enriched in organics, mostly plant materials that derive their ^{199}Hg and ^{201}Hg depletion from the atmosphere and they overwhelm the proportion of enriched ^{199}Hg and ^{201}Hg signature that is represented by adsorped Hg(II) from water. 2. in situ MeHg produced by bacterial activity might have a depleted odd N Hg isotopic signature. This could explain higher magnitude of depletion with increasing depth of sediment indicating higher microbial activities over time. 3. adsorption of Hg(II) on particles fractionates Hg isotopes, though this process seems least likely. To resolve the issue, future work involves analysis of more lake, river, estuary and deep ocean sediments where the proportion of organics is variable. At the same time bacteria generated MeHg needs to be measures for Hg isotopes.