Fractionated Mercury Isotopes in Fish: The Effects of Nuclear Mass, Spin, and Volume

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Introduction
Mercury is long known as a common environmental contaminant. In methylated form it is even more toxic and the methylation process is facilitated by microbial activities. Methyl mercury easily crosses cell membrane and accumulates in soft tissues of fishes and finally biomagnifies with increasing trophic levels. Natural variations in the isotopic composition of mercury have been reported and such variations have emphasized mass dependent fractionations, 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 the soft tissues of fishes.

Experiment
Approximately 1 gm of fish sample was dissolved in 5 ml of aqua regia for 24 hours and filtered. The sample solution was diluted and reduced with SnCl₂ in a hydride generator and Hg(0) vapor was measured in a Thermo-Finnigan Neptune MC-ICPMS. To minimize effects of instrumental fractionation isotope ratios were measured by sample standard bracketing and reported as $\delta$ (%o) relative to NIST SRM 3133 Hg standard where $\delta^{\text{AHg}} = [(^{\text{AHg}}/^{\text{202Hg}})_{\text{sample}}/(^{\text{AHg}}/^{\text{202Hg}})_{\text{NIST3133}}] - 1 \times 1000$ %o.

Results and Discussion
In this study we have measured the isotope ratios $^{198}$Hg/$^{202}$Hg, $^{199}$Hg/$^{202}$Hg, $^{200}$Hg/$^{202}$Hg, $^{201}$Hg/$^{202}$Hg, $^{204}$Hg/$^{202}$Hg. In all the fish samples $\delta^{198}$Hg, $\delta^{200}$Hg, $\delta^{202}$Hg, $\delta^{204}$Hg falls along a straight line defining the mass dependent fractionation of the even isotopes where as the odd isotopes $\delta^{199}$Hg and $\delta^{201}$Hg plots above the fractionation line. The magnitude of the deviation ($\Delta$Hg where n=199 or 201) obtained by difference between the measured $\delta^{199}$Hg and $\delta^{201}$Hg of the samples and the value obtained by linear scaling defined by the even-mass isotopes ranges from approximately 0.2 %o to 3 %o (Figure 1).

Discussion
MIF of mercury can be caused by the nuclear volume effect. Schauble, 2007 has calculated nuclear volume fractionation scaling factors for a number of common mercury chemical species in equilibrium with Hg⁰ vapor. From his calculations the nuclear field shift effect is larger in $\Delta^{199}$Hg than in $\Delta^{201}$Hg by approximately a factor of two. The predominant mercury chemical species in fish is methylmercury cysteine. Enrichment of $^{199}$Hg and $^{201}$Hg at the thionyl functional groups of cysteine is what could be predicted from the experimental studies of Buchachenko and others (2004) on the reaction of methylmercury chloride with creatine kinase. Here the magnetic isotope effect (MIE) produces a kinetic partial separation of isotopes with non-zero nuclear spin quantum numbers from the even-N isotopes. The ratio of enrichment of $\Delta^{201}$Hg/$\Delta^{199}$Hg is predicted from theory to be 1.11, which is the ratio of the magnetic moments of $^{199}$Hg and $^{201}$Hg.

Conclusions
Because mercury possesses two odd-N isotopes, it is possible to detect and evaluate the effects of two distinct, mass-independent isotope fractionating processes. From the data obtained on fish samples, we can deconvolute the contributions of the isotope effects of nuclear mass, spin, and volume. For these samples the role of spin or the magnetic isotope effect is the most dominant.

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References