In Vivo Mass-independent Fractionation of Mercury Isotopes in Fish

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Introduction

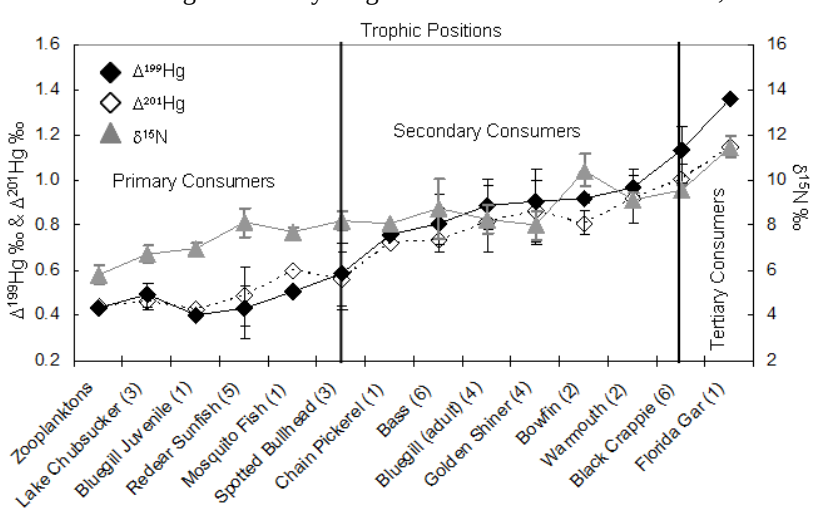
Recent experimental work and analyses of natural samples have revealed both mass-dependent and mass-independent isotope fractionation effects in mercury. These findings portend new avenues toward understanding the global mercury cycle. It has been shown experimentally that photo reduction of Hg^{+2} and methylmercury in water with concomitant release of the reduced, gaseous species Hg^{o} results in the residual methylmercury possessing a mass-independent isotope effect. This effect is a relative enrichment of isotopes ^{199}Hg and ^{201}Hg over the even mass number isotopes when compared to the mercury standard NIST SRM3133. Large mass independent fractionation (MIF) effects ($\Delta^{199}Hg$ values of a few permil) have been found in mercury in fish and interpreted as isotope effects inherited from the water. To evaluate the possibility that MIF might be produced within the fish, we have analyzed 38 samples that include zooplankton and twelve different species of fish from a single lake collected over a 2-month time period for mercury isotopic compositions. Trophic levels of the same fish specimens had previously been determined from stomach contents and nitrogen isotopes.

Experiment

Approximately 100 mg of freeze dried fish sample (muscle tissue) was dissolved in 5 ml of aqua regia for 24 hours and filtered. The sample solution was diluted and reduced with $SnCl_2$ 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 δ (‰) relative to NIST SRM 3133 Hg standard where $\delta^{A}Hg = [(^{A}Hg/^{202}Hg)_{sample}/(^{A}Hg/^{202}Hg)_{NIST3133}] - 1 \times 1000\ ^{o}/_{oo}$ Values $\Delta^{199}Hg$ and $\Delta^{201}Hg$ are defined as the difference between the measured $\delta^{199}Hg$ and $\delta^{201}Hg$ of the samples and the value calculated based on the even-mass isotopes abundances and mass-dependent fractionation law ($\delta^{199}Hg_{MDF}$). $\Delta^{199}Hg_{MIF} = \delta^{199}Hg_{MEASURED} - \delta^{199}Hg_{MDF}$.

Results

Zooplankton in the lake contain mercury with $\Delta^{199}Hg$ and $\Delta^{201}Hg$ values of +0.43 and +0.44 respectively. Among the fish species there is a striking correspondence between trophic level and $\Delta^{199}Hg$ and $\Delta^{201}Hg$ values for primary, secondary, and tertiary consumers. The $\Delta^{199}Hg$ values ranges over ~1‰ from ~+ 0.4 in zooplankton, juvenile bluegill and several other small fishes to $\Delta^{199}Hg$ = + 1.36 (Figure 1) for the Florida gar that is the top predator fish in the lake. These observations indicate that the MIF effect, rather than being an artifact of the water column is produced *in vivo*.

Discussion

Partial separation of ^{199}Hg and ^{201}Hg from isotopes of even neutron number can be achieved by the magnetic isotope effect in reactions involving sufficiently long-lived intermediate free radicals, where nuclear – electron hyperfine coupling influences radical recombination and thus reaction kinetics. There is experimental evidence that this can occur during the inhibiting activity of methylmercury on creatine kinase. Here the enzyme provides the free radicals. Previously reports of chemical mass-independent fractionation of isotopes in nature have involved gas phase reactions and largely explained by photolysis. It now seems that isotopic MIF can occur during metabolic processes as well.