Mass-independent fractionation of Hg isotopes by biological processes

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Variations in the stable isotope composition of mercury (Hg) in food web organisms (crustaceans, forage fish, and top predator fish) and sediment cores from three different lakes were measured by multicollector inductively coupled plasma mass spectrometry (performed by Activation Laboratories Ltd.). Total Hg and methylmercury (MeHg) analyses were done as well. Our purpose was to investigate possible biotic fractionation of Hg isotopes. The $^{198}Hg/^{202}Hg$, $^{199}Hg/^{202}Hg$, $^{200}Hg/^{202}Hg$, and $^{201}Hg/^{202}Hg$ ratios of Hg in standard solutions and sample digests (adjusted to concentrations of 2-5 $ng \cdot mL^{-1}$ and analysed in the order standard-sample-standard following reduction of Hg(II) to Hg(0) with $SnCl_2$) were used to calculate $\delta^{198}Hg$, $\delta^{199}Hg$, $\delta^{200}Hg$, and $\delta^{201}Hg$ values.

Evidence for mass-independent fractionation of Hg isotopes with odd mass numbers (^{199}Hg and ^{201}Hg) was found in the biotic assemblages from all three lakes, but only mass-dependent effects were observed in the sediments. Thus, in plots of $^{198}Hg/^{202}Hg$ against $^{200}Hg/^{202}Hg$ the organisms and sediments formed a single linear regression line, but plots of $^{199}Hg/^{202}Hg$ and $^{201}Hg/^{202}Hg$ against $^{200}Hg/^{202}Hg$ showed that the organisms were anomalously rich in ^{199}Hg and ^{201}Hg relative to sediments. Similarly, the $\delta^{199}Hg$ and $\delta^{201}Hg$ values of each biotic assemblage were higher than $\delta^{198}Hg$ and $\delta^{200}Hg$ and had a different pattern of variation. The deviations of the $^{199}Hg/^{202}Hg$ and $^{201}Hg/^{202}Hg$ ratios of the organisms, and the corresponding $\delta^{199}Hg$ and $\delta^{201}Hg$ values as well, increased with MeHg concentration, whereas $\delta^{198}Hg$ and $\delta^{200}Hg$ gave inverse correlations. Analysis of MeHg and inorganic Hg fractions of fish proved that MeHg was highly enriched in ^{199}Hg and ^{201}Hg, as implied by the data for whole organisms. Moreover, isotopic signatures of organisms showed effects of habitat and diet (e.g. isotopic differences between planktonic and benthic crustaceans and fish that prey on them) and a distinctive anomaly found consistently in lake whitefish.

We conclude that biological processes involved in the biogeochemical cycle of MeHg in aquatic ecosystems mediate mass-independent fractionation of Hg isotopes. This phenomenon is attributable to effects of nuclear spin and penetration of the inner electron shells of Hg by valence electrons of ligands owing to the high nuclear charge of Hg and inefficient shielding of it by *d*- and *f*-electrons.