Hg Stable Isotope Measurements in Fish Tissue as Indicators of Hg Chemical Transformations in East Fork Poplar Creek, TN

Student abstract

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Mercury (Hg) is a highly toxic heavy metal with complex biogeochemical cycling. Hg occurs in two chemical forms in the environment; Hg(0) which is insoluble, and less toxic, and Hg(II), the highly soluble and reactive form of Hg. The complex biogeochemical cycle of Hg complicates our understanding of Hg interactions in contaminated DOE sites. The East Fork Poplar Creek (EFPC), which flows from the DOE Y-12 complex near Oak Ridge, TN, and empties into the Clinch River in Tennessee, has been contaminated by historic Hg emissions from the plant. Remediation efforts have reduced the Hg input into the creek significantly; however, methylmercury (MeHg) concentrations in the water and fish have not decreased.

Hg stable isotope measurements provide a unique potential to identify and quantify sources and chemical transformations of Hg, such as breakdown of MeHg and reduction of Hg(II) to Hg(0). Hg has seven stable isotopes (^{196}Hg, ^{198}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, ^{202}Hg, ^{204}Hg). There are two known mechanisms to alter the relative abundances of the Hg isotopes. One, the kinetic isotope effect (KIE), enriches the product of Hg(II) reduction, methylation, demethylation and a few other processes, with lighter Hg isotopes relative to the reactant pool. This mass dependent fractionation (MDF) mechanism is due to the fact that lighter isotopes tend to react more readily than heavier isotopes. The second mechanism to alter the relative abundances of Hg isotopes is mass independent fractionation (MIF). Studies have shown that photochemical transformations of Hg cause the odd isotopes of Hg to act differently than what theoretical calculations based on MDF would predict. This effect, known as the magnetic isotope effect, allows ^{199}Hg and ^{201}Hg to back-react during photochemical reactions, and get depleted in the product of a reaction. The relative abundances of Hg isotopes are reported relative to NIST SRM 3133, an accepted inter-laboratory standard.

We analyzed fish tissue taken from upstream (close to the Y-12 complex) and downstream (18.5 km downstream from the plant) of the EFPC. The measured ^{202}Hg/^{198}Hg ratios show a weak positive trend from -0.59±0.06‰ (n=4) upstream to -0.31±0.14‰ (n=4) downstream. Fish are believed to be integrators of Hg over time, so the positive trend they exhibit may be indicative of some chemical transformation of Hg in the EFPC waters. Odd isotope anomalies were also detected in the fish samples. The slope calculated when the ^{199}Hg anomalies are plotted against the ^{201}Hg anomalies is consistent with previous studies' observations of photochemical MeHg reduction to Hg(0). Overall, the results suggest that the Hg taken up by the fish has experienced little redox cycling, and specifically we see no evidence for extensive Hg(II) reduction or photochemical demethylation.