Mercury Isotopic Signature of the Atmosphere

S.Ghosh and A.L. Odom (FSU Geological Sciences and NHMFL Geochemistry)

Introduction

The atmosphere has the cardinal role in the global dispersion and deposition of mercury. Mercury enters and leaves the atmosphere through a myriad of processes both natural and anthropogenic. Even as their relative importance can be debated, the processes involved in the introduction of mercury into the atmosphere are perhaps better understood than the physiochemical mechanisms of its removal. Of the total atmospheric mercury inventory, elemental vapor contributes 98%. If its residence time (estimated in the range of 0.5 to 2.0 years) is significantly longer than a troposphere mixing time (estimated to be one month), the atmosphere might come close to an isotopically uniform reservoir of mercury (IUR)\(^{199}\)Hg, on which local and temporary effects are likely imposed. The existence of an (IUR)\(^{199}\)Hg might be the anchor around which models of the global mercury cycle could be constrained. Previously we reported measurements of the isotopic composition of atmospheric mercury trapped in the epiphyte Tillandsia Usenoides (Spanish moss). When normalized to the NIST-3133 standard and corrected for mass-dependent fractionation, Hg from the moss samples exhibit a depletion of the odd neutron number isotopes \(^{199}\)Hg and \(^{201}\)Hg. Because \(^{199}\)Hg and \(^{201}\)Hg are depleted in nearly equal amounts, we attributed this mass-independent fractionation (MIF) to a magnetic isotope effect (MIE) in accordance with the nearly equal nuclear magnetic moments of the two odd A isotopes. In this study we present results of mercury isotopic analysis of elemental mercury collected from ambient air mass.

Experiment

A refined procedure permitting precise isotopic analyses of as little as 7ng of mercury has made it possible to characterize atmospheric mercury vapour directly. The Mercury is trapped on gold plated sand in a quartz tube. Air is passed through this gold trap by a pump, and a flow meter with an adjustable needle valve is used to control and measure the flow rate. Once the sampling is complete, mercury is thermally purged from the gold trap, and carried by a helium stream into concentrated nitric acid containing chloride, where it is completely oxidized to Hg (II). At a concentration of 1ppb the Hg (II) is reduced in a hydride generator, and the evolving cold mercury vapour is analyzed in a NEPTUNE MC-ICP-MS.

Results

In the area from the city of Tallahassee, Florida, to the Gulf of Mexico, multiple samples of atmospheric mercury exhibits a mass dependent fractionation effect with light isotope enrichment in \(^{198}\)Hg/\(^{202}\)Hg ratios (relative to NIST-SRM 3133) of 1.5 to 2.5 ‰, and small but reproducible mass independent fractionation effects with positive \(^{199}\)Hg and \(^{201}\)Hg anomalies of +0.1 to +0.3 ‰.

Discussion and Conclusions

This study demonstrates a marked difference between the mercury isotopic composition of the epiphyte Spanish moss and the ambient air mass. Relative to the NIST SRM-3133 standard, mercury measured in atmospheric samples have marginally positive \(^{199}\)Hg and \(^{201}\)Hg values, while epiphyte samples have clearly negative \(^{199}\)Hg and \(^{201}\)Hg values. This suggests that the moss is either trapping mercury from a pathway other than direct atmospheric deposition, or the MIF observed may be a result of enzyme activity within the moss. Ongoing research will allow us to choose between the alternatives.

Our global network of air collection sites also promises to shed some more light on the scale of isotopic homogeneity/heterogeneity (local, regional, hemispherical, global) of atmospheric mercury.