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INVESTIGATION OF MERCURY ISOTOPIC FRACTIONATION AS A NOVEL TRACER  
FOR SOURCES AND PATHWAYS OF MERCURY IN THE ENVIRONMENT.

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In contrast to other heavy metals in the environment, Hg can be singled out as a truly global pollutant with very unique chemical properties. Atmospheric transport from both natural and anthropogenic sources occurs in the vapor phase with a residence time of at least one year. Hg is the only heavy metal, which indisputably biomagnifies through the food chain even in remote areas. However, the relative importance of natural vs. anthropogenic sources in many areas is poorly understood. In terms of local and global transport and deposition rates many questions remain with regard to relative importance of elemental mercury ( $\text{Hg}^0$ ), reactive gaseous mercury (RGM), and particulate mercury. Flux measurements of mercury into and out of the atmosphere are further complicated by a number of chemically and biologically mediated reactions. Aerobic and anaerobic bacterial processes can transform  $\text{Hg(II)}$  into  $\text{Hg(0)}$ , methyl mercury (MeHg),  $\text{HgS}$ , etc., which impacts its biogeochemical cycling. A novel approach to investigate the sources of mercury pollution as well as the pathways and degree of reprocessing is the determination of isotopic fractionation signatures of the seven mercury isotopes. Stable isotope fractionation of lower mass systems such as H, C, N, O, and S has been investigated for the past 30 years. For heavy isotope systems such as mercury (amu 196-204) the degree of mass fractionation is very small and is basically impossible to measure with traditional mass spectrometric methods for small sample amounts. Only for the past few years multi-collector inductively couple plasma mass spectrometry (MC-ICP-MS) has established itself as a reliable and robust method to measure isotopic fractionation of non-traditional isotope systems at precision levels down to 0.002% (20 ppm, 2s). Using a new, state-of-the-art NU Plasma MC-ICP-MS we have developed a method that allows the routine measurement of the mercury isotopic composition for samples sizes of less than 100ng Hg at a precision of 0.003%. The isotopic composition of mercury in the solar system in general and on earth in particular was poorly characterized. Before any valid conclusions about possible isotopic signatures for various natural systems and anthropogenic sources can be drawn, we started to investigate the isotopic composition of primitive meteorites, which reflect the composition of the early solar nebular. Despite earlier reports of certain large anomalies our study of 20 carbonaceous meteorites confirmed that all solar mercury is isotopically similar to mercury found in terrestrial sources. In detailed studies of various ore deposits we established that the degree of mercury isotopic fractionation within different boiling zones of single deposits spans a range of over 0.1% per amu or 0.5% for the  $^{198}\text{Hg}/^{202}\text{Hg}$  isotope ratio (100times larger than the analytical resolution). The analysis of various organic materials such as fish, lobster, human hair, leaves, and sediments show fractionation spanning 0.02 – 0.07 %/amu. Initial mechanistic studies of fractionation during methylation by anaerobic sulfate reducing bacteria cultures under optimal growth conditions did not exceed 0.03%/amu. Mechanistic studies of isotopic fractionation by various bacterial processes will be investigated in detail under realistic conditions. Sampling efforts for important point sources such as coal fired power plants and waste incinerators are underway. Several sediment cores from lakes and rivers in the vicinity of point sources such as a tannery, chlorine-alkali plant, and heavy industry

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have been obtained. Historical records of global mercury pollution in peat bog cores from remote sites in southern Chile will reveal if there is a measurable anthropogenic isotopic signature.