MERCURY CONCENTRATION AND SPECIATION IN COASTAL RAINWATER

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ABSTRACT

Mercury exists in mainly two oxidation states in the atmosphere, Hg^0 and Hg(II). Inorganic divalent mercury, Hg(II), has a greater solubility; therefore is in higher concentration in rainwater, than Hg^0. The toxic species, methylmercury is an organic form of Hg(II) and is present in low concentration. Mercury is released into the atmosphere by natural and anthropogenic sources. Rainwater is thought to be a main removal mechanism for atmospheric mercury. The concentration and speciation of mercury were determined in rainwater from Wilmington, NC, from September 1, 2003 to September 30, 2005. Volume weighted averages for total Hg in unfiltered rainwater, total dissolved Hg, particulate Hg, dissolved gaseous Hg (Hg^0) and methyl-Hg were 52.9 ± 4.7 pM, 40.6 ± 4.0 pM, 13.7± 1.5 pM, 4.3 ± 0.9 pM and 1.1 ± 0.1 pM, respectively.

All mercury species were present in all seasons with no significant difference in concentrations between summer and winter, except dissolved gaseous mercury concentration was higher in the winter, with a higher ratio of Hg(II)/Hg(0) in summer relative to winter events. Diurnal variation was seen where Hg(II) decreased during the day into the night, suggesting photochemical reduction of Hg(II). All Hg concentrations were higher in continental storms relative to coastal rain events. Both total mercury species (UFHg and TDHg) were positively correlated with particulate mercury. Total mercury species were washed out of the atmosphere by rainwater with lower concentrations for larger rain events. A weak positive correlation was observed between TDHg and NO_3^-, TDHg and SO_4^{2-}, DGHg and Cl^-, and Hg_{part} and DOC.

The photochemistry of mercury from Wilmington was also investigated. UFHg, TDHg, and DGHg were generally produced upon irradiation of rainwater samples by

simulated sunlight. Particulate Hg concentrations generally declined upon irradiation and MMHg concentrations showed no pattern, in some instances, increasing, decreasing or remaining the same. Positive correlation was observed between, production of UFHg and Hg_{part} and a negative correlation was observed between production of TDHg and Hg_{part}. Continental events increased in Hg_{part} while decreasing in TDHg, whereas coastal events increased in TDHg while decreasing in Hg_{part} after irradiation. Seasonal differences between Hg species were similar with an increase in TDHg and DGHg, while decreasing in Hg_{part} and greater changes were observed during the winter. Diurnal variations of Hg(II)/Hg(0) ratio increased during the afternoon and decreased there after.

Atmospheric global inputs by natural and anthropogenic sources, 4.1×10^6 kg or 2.0×10^7 mol per year, were in good agreement with calculated total flux of mercury removed via wet deposition, 3.8×10^6 kg or 1.9×10^7 mol per year, suggesting that essentially all mercury released into the atmosphere is removed via rain.

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