

MERCURY CONCENTRATION AND SPECIATION  
IN COASTAL RAINWATER

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## ABSTRACT

Mercury exists in mainly two oxidation states in the atmosphere,  $\text{Hg}^0$  and  $\text{Hg(II)}$ . Inorganic divalent mercury,  $\text{Hg(II)}$ , has a greater solubility; therefore is in higher concentration in rainwater, than  $\text{Hg}^0$ . The toxic species, methylmercury is an organic form of  $\text{Hg(II)}$  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 ( $\text{Hg}^0$ ) and methyl-Hg were  $52.9 \pm 4.7$  pM,  $40.6 \pm 4.0$  pM,  $13.7 \pm 1.5$  pM,  $4.3 \pm 0.9$  pM and  $1.1 \pm 0.1$  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  $\text{Hg(II)}/\text{Hg(0)}$  in summer relative to winter events. Diurnal variation was seen where  $\text{Hg(II)}$  decreased during the day into the night, suggesting photochemical reduction of  $\text{Hg(II)}$ . 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  $\text{NO}_3^-$ , TDHg and  $\text{SO}_4^{2-}$ , DGHg and  $\text{Cl}^-$ , and  $\text{Hg}_{\text{part}}$  and DOC.

The photochemistry of mercury from Wilmington was also investigated. UFGHg, 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,  $4.1 \times 10^6$  kg or  $2.0 \times 10^7$  mol per year, were in good agreement with calculated total flux of mercury removed via wet deposition,  $3.8 \times 10^6$  kg or  $1.9 \times 10^7$  mol per year, suggesting that essentially all mercury released into the atmosphere is removed via rain.

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