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ABSTRACT

Copper exists in two oxidation states in natural waters, Cu(I) and Cu(II). Determining the speciation of copper rather than its total concentration is essential in order to assess the atmospheric reactivity and environmental fate of copper in the troposphere. The concentration and speciation of copper was determined in rainwater samples from Wilmington, North Carolina, from August 25, 2000 to September 24, 2002. Volume weighted average concentrations of Cu_{total}, Cu(I), and Cu(II) in rainwater were 5.3 nM, 1.4 nM, and 3.2 nM, respectively. An undetermined ligand may be stabilizing Cu(I) in authentic rainwater.

Rainwater Cu(II) concentrations were significantly higher in the summer, whereas Cu(I) concentrations were significantly higher in the winter. The calculated atmospheric flux of copper, 504 $\mu g\ m^{-2}\ yr^{-1}$, is in good agreement with the calculated copper flux at Florianopolis, Brazil and two Maryland Chesapeake Bay sites. Copper(I) and Cu(II) concentrations were not correlated with each other and Cu(II) concentrations did not correlate with any other rainwater analyte. Significant positive correlations were found between Cu(I) and DOC, SO_4^{2-}, NO_3^-, and Fe_{total}. All copper species (Cu(I), Cu(II), Cu_{total}, $Cu_{particulate}$) showed an inverse correlation with rainfall amount. All copper species increased in concentration with decreasing rainwater pH. All copper species were higher for storms of continental origin versus storms of coastal origin. No diurnal variations were seen with Cu(I). However, Cu(II) concentrations had a maximum between 12 pm – 6 pm. It is possible that Fe oxyhydroxides with adsorbed Cu(II) undergo reactions that release Cu(II) in the presence of sunlight.

Contamination by trace metals, such as copper, contributes to the degradation of estuarine systems in many areas, including North Carolina. Speciation, or the distribution of copper among its various chemical forms, controls the reactivity, toxicity, and bioavailability of the metal in estuarine sediments and water, as in rain. Estuarine water samples were collected and analyzed for Cu(I) during April, July, and November of 2001 and March 2002. The percentage of total copper as Cu(I) varied from 1.9% - 4.1% with an overall average of 3.4%. No flux of Cu(I) was observed into or out of the water overlying the estuarine sediments in controlled laboratory experiments. Almost the same amount of copper that enters the Cape Fear River estuary from atmospheric deposition (8.7×10^2 moles Cu/year) fluxes into the sediments (5.8×10^2 moles Cu/year).

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