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INTERACTIONS BETWEEN DISSOLVED ORGANIC MATTER AND MERCURYGeorge Aiken and Mike Reddy

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Interactions of mercury (Hg) with dissolved organic matter (DOM) play important roles in controlling reactivity, bioavailability and transport of Hg in aquatic systems. To better define the nature and magnitude of these interactions, the hydrophobic acid fraction (HPOA), hydrophilic acid fraction (HPIA), fulvic acid and humic acid were isolated from surface waters in the Florida Everglades using XAD resins. These isolates and whole water samples were used to study interactions of DOM with Hg in cinnabar (HgS) dissolution and precipitation experiments under a range of pH and concentration conditions. In addition, interactions of Hg with DOM were studied via Schubert's method, an ion-exchange technique designed to yield information on Hg-DOM binding constants.

Cinnabar is a relatively insoluble solid ($\log K_{sp} = -52.4$) under most environmental conditions. Organic matter isolated from the Everglades was reacted with cinnabar for a period of seven days at pH 6.0. Dissolved Hg concentrations, measured on a cold vapor atomic absorption spectrophotometer, were below the detection limit (<2.5 nM) in the absence of organic matter. In the presence of DOM, particularly the humic fractions (HPOA, humic acid, and fulvic acid), a significant amount of Hg (up to 1.7 $\mu\text{M}/\text{mg C}$) was released from cinnabar suggesting strong interactions. The amount of Hg dissolved by various fractions of organic matter followed the order: humic acid $>$ HPOA \cong fulvic acid \gg HPIA. The hydrophobic and hydrophilic neutral fractions dissolved

insignificant quantities of Hg from cinnabar. Model compounds such as cysteine and thioglycolic acid dissolved small amounts of Hg from the cinnabar surface, while other model compounds such as acetate, citrate, and EDTA dissolved no detectable Hg. There was a positive correlation ($R^2 = 0.84$) between the amount of Hg released and the aromatic carbon content (determined by ^{13}C -NMR). Cinnabar dissolution experiments indicated a strong interaction between organic matter and mercury.

Precipitation and aggregation of metacinnabar (black HgS) was inhibited in the presence of low concentrations (≤ 3 mg C/L) of humic fractions of dissolved organic matter (DOM) isolated from the Florida Everglades. At low Hg concentrations ($\leq 5 \times 10^{-8}$ M), DOM prevented the precipitation of metacinnabar. At moderate Hg concentrations (5×10^{-5} M), DOM inhibited the aggregation of colloidal metacinnabar (Hg passed through a $0.1 \mu\text{m}$ filter, but was removed by centrifugation). At Hg concentrations greater than 5×10^{-4} M, mercury formed solid metacinnabar particles that were removed from solution by a $0.1 \mu\text{m}$ filter. Organic matter rich in aromatic moieties was preferentially removed with the solid. HPOA, humic and fulvic acids inhibited aggregation better than HPIA. Chloride, acetate, salicylate, EDTA, and cysteine did not inhibit the precipitation or aggregation of metacinnabar. Calcium enhanced metacinnabar aggregation even in the presence of DOM; the magnitude of the effect was dependent on the concentrations of DOM, Hg, and Ca^{+2} . Inhibition of metacinnabar precipitation appears to be the result of strong DOM-Hg binding. Prevention of aggregation of colloidal particles appears to be caused by adsorption of DOM and electrostatic repulsion.

Finally, the strength of DOM – Hg binding interactions was investigated using an ion-exchange resin (Schubert's) method. We compared the distribution ratios for mercury between the resin and water ($[\text{Hg}_{\text{resin}}]/[\text{Hg}_{\text{soln}}]$) in the presence of organic matter isolates and several inorganic (chloride, bromide) and organic (citric, EDTA, thioglycolic acid) ligands with known Hg-ligand stability constants. The distribution ratio is inversely related to the binding strength between the ligand and Hg. We observed much smaller distribution ratio values in the presence of HPOA isolates than in the presence of ligands with strong binding properties such as EDTA (log K for Hg-EDTA complexes is 23.0). The distribution ratios determined in the presence of the HPOA isolates were comparable to those obtained for the most strongly binding ligand, thioglycolic acid ($\beta = 10^{30}$) suggesting similar reduced sulfur binding sites in both. The HPOA isolates bound mercury more strongly than the HPIA fraction.