

## Interactions between dissolved organic matter and mercury in the Florida Everglades

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**Abstract.** Experiments were conducted using organic matter isolated from various surface waters in the Florida Everglades to study the interactions between dissolved organic matter (DOM) and Hg(II). Conditional distribution coefficients ( $K_{DOM}$ ), obtained using an equilibrium dialysis ligand exchange method, were strongly affected by the Hg/DOM concentration ratio. Very strong interactions ( $K_{DOM} = 10^{13.2-15.5} \text{ L kg}^{-1}$ ), indicative of Hg-thiol bonds, were observed at Hg/DOM ratios below approximately 1  $\mu\text{g Hg}$  per mg DOM. Above approximately 10  $\mu\text{g Hg}$  per mg DOM much lower  $K_{DOM}$  values ( $10^{10.7-10.5} \text{ L kg}^{-1}$ ) were obtained. DOM-Hg interactions were also studied by HgS ( $\log K_{sp} = -52.4$ ) dissolution and precipitation experiments. In the dissolution experiments, a significant amount of Hg was released from cinnabar in the presence of DOM, suggesting strong interactions. Conversely, precipitation of HgS was strongly inhibited in the presence of low concentrations ( $\leq 3 \text{ mg C/L}$ ) of DOM. In both the dissolution and precipitation experiments, organic matter rich in aromatic moieties was more reactive with HgS than less aromatic fractions and sulfur-containing model compounds. These results suggest that DOM can influence the geochemistry of inorganic complexes of Hg in the Everglades, especially HgS, by strong Hg-DOM binding and colloidal stabilization.

### 1. Introduction

It is well recognized that the chemical forms of Hg in the water column and sediments are intimately related to its overall effects on living organisms. Interactions of Hg with dissolved organic matter (DOM) are hypothesized to play important roles in controlling the reactivity, bioavailability and transport of Hg in the Everglades. Little is known, however, about the mechanisms and strength of Hg interactions with DOM. In numerous studies of northern temperate environments, strong correlations have been noted between the concentration of Hg and DOM concentration in ground, lake and stream waters. In the Everglades, however, no correlation exists between these two species. This difference is likely due to differences in the sources, cycling and transport of these species in the Everglades compared to other systems. Hg, which is atmospherically deposited, is found in relatively low concentrations ( $< 5 \text{ ng/L}$ ) throughout the Everglades (1), whereas, DOM and particulate organic matter (POM), produced in situ and transported in surface and peat pore waters, are found in high concentrations.

The most significant processes to define for understanding the chemistries of organic matter and Hg in the Everglades are the effects of DOM on the chemical speciation and bioavailability of Hg in the sediments of the system, the effects of DOM on the partitioning of Hg and MeHg between dissolved and particulate phases and the biota in the water column, and the effects of DOM on the photoreactivity of Hg and MeHg. The speciation of  $\text{Hg}^{+2}$  in aquatic systems depends, in large part, on pH, DOM concentration, the concentrations of inorganic ligands, especially sulfide ( $\text{S}^{-2}$ ), and the distribution of  $\text{Hg}^{+2}$  between dissolved and particulate phases. Of particular significance are the

interactions of DOM with  $\text{Hg}^{+2}$  in the presence of  $\text{S}^{-2}$  at the sediment water interface. To better define the nature and magnitude of these interactions, experiments were designed using organic matter isolated from various surface waters in the Florida Everglades to determine Hg-DOM binding constants and to study the interactions between DOM and cinnabar ( $\text{HgS}$ ). The isolates, obtained using XAD resins (2), exhibited a wide range of elemental compositions, aromatic carbon contents, reduced sulfur contents, and molecular weights. Chemical composition of the DOM, especially aromatic carbon and reduced sulfur functional group content, was found to be important in controlling DOM interactions with  $\text{Hg(II)}$ .

## 2. RESULTS

### 2.1 Hg-DOM Binding Interactions

While DOM has been implicated as an important class of compounds controlling the fate and transport of Hg in aquatic systems, reliable binding constants ( $\log K$ ), indicators of the strength of DOM – Hg binding interactions, are unavailable. Determination of these constants is hampered by the intrinsic complexity of the DOM itself, by the lack of stoichiometric information, and by the difficulties presented in determining appropriate binding constants at the low Hg:DOM conditions that exist in most aquatic systems, including the Everglades. We modified an equilibrium dialysis ligand exchange method (3,4,5) to determine Hg-DOM binding constants over a wide range of Hg to DOM concentration ratios. Very strong interactions ( $K_{\text{DOM}}' = 10^{23.2 \pm 0.5} \text{ L kg}^{-1}$  at  $\text{pH} = 7.0$  and  $I = 0.1$ ), indicative of Hg-thiol bonds, were observed at Hg/DOM ratios below approximately  $1 \mu\text{g Hg per mg DOM}$ . Hg/DOM ratios above approximately  $10 \mu\text{g Hg per mg DOM}$  gave much lower  $K_{\text{DOM}}'$  values ( $10^{10.7 \pm 0.5} \text{ L kg}^{-1}$  at  $\text{pH} = 4.9$  to  $5.6$  and  $I = 0.1$ ), consistent with Hg binding mainly to oxygen functional groups.

Strong evidence for the participation of reduced-S functional groups in the binding of  $\text{Hg}^{+2}$  by natural organic matter has been demonstrated in spectroscopic studies (6,7). Based on elemental analyses and X-ray adsorption near edge spectroscopy measurements, the DOM sample from the Everglades used in our binding experiments had a reduced-S content of approximately 1.0 wt %. A 1 mg/L solution of the isolate therefore contains a reduced-S concentration of  $3.2 \times 10^{-7} \text{ M}$ . We found that only a small fraction (approximately 2%) of the reduced-S groups were involved with the strongest interactions between Hg and DOM. These results agree well with data reported for the binding of methylmercury with Suwannee River humic acid (8) and suggest that the binding of Hg to DOM under natural conditions (very low Hg/DOM ratios ranging from 0.01 to 10 ng of Hg/mg of DOM) is controlled by a small fraction of DOM molecules containing reactive thiol functional groups.

Under most environmental conditions, therefore, it can be expected that only the strongest DOM sites will interact with  $\text{Hg}^{+2}$ . In the case of fully oxygenated Everglades water (sulfide-free), the binding of  $\text{Hg}^{+2}$  by DOM should dominate Everglades' dissolved inorganic mercury speciation. However, even for the case of strong binding sites ( $K_{\text{DOM}}' = 10^{23.2 \pm 0.5} \text{ L kg}^{-1}$ ), Hg-sulfide complexes should dominate dissolved inorganic Hg solution speciation in the presence of small concentrations (nanomolar) of sulfide because of the strong sulfide affinity for Hg. Where measurable total sulfide concentrations are present in the surface water and pore water of the Everglades, therefore, Hg-sulfide complexes likely predominate.

### 2.2 DOM-HgS Interactions

Benoit and others (9) have hypothesized that neutral forms of  $\text{HgS}$  ( $\text{HgS}^0$ ) are more likely to partition across cell membranes than charged species; however, a chemical equilibrium approach may not completely explain the speciation and behavior of  $\text{Hg(II)}$  in the presence of DOM. For instance, chemical speciation models indicate that pore waters in the Everglades, especially in the eutrophic areas, are supersaturated with respect to cinnabar ( $\text{HgS}$ ). Even though geochemical speciation models

predict its formation, no cinnabar has been found in the peat soils of the Everglades (Gilmour, personal communication). To better define the geochemical interactions between DOM,  $\text{Hg}^{+2}$  and  $\text{S}^{-2}$ , experiments were designed using organic matter isolates and whole water samples to study interactions of DOM with Hg in cinnabar dissolution and precipitation experiments under a range of pH and concentration conditions. Cinnabar is a relatively insoluble solid ( $\log K_{sp} = -52.4$ ) under most environmental conditions.

Cinnabar dissolution experiments indicated strong interactions between organic matter and mercury (10). 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 ( $<2.5 \text{ nM}$ ) in the absence of organic matter. In the presence of DOM a significant amount of Hg (up to  $1.7 \text{ } \mu\text{M/mg C}$ ) was released from cinnabar. The amount of Hg released into solution varied with DOM fraction, following the order: humic acid > hydrophobic organic acid fraction (HPOA)  $\cong$  fulvic acid  $\gg$  hydrophilic organic acid fraction (HPIA). Insignificant quantities of Hg were released in the presence of the hydrophobic and hydrophilic fractions of the DOM. 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 of the dissolved organic matter fractions (determined by  $^{13}\text{C-NMR}$ ).

Precipitation and aggregation of metacinnabar (black  $\text{HgS}$ ) was inhibited in the presence of low concentrations ( $\leq 3 \text{ mg C/L}$ ) of humic fractions of dissolved organic matter (DOM) isolated from the Florida Everglades (11). At low Hg concentrations ( $\leq 5 \times 10^{-8} \text{ M}$ ), DOM prevented the precipitation of metacinnabar. At moderate Hg concentrations ( $5 \times 10^{-5} \text{ M}$ ), DOM inhibited the aggregation of colloidal metacinnabar (Hg passed through a  $0.1 \text{ } \mu\text{m}$  filter, but was removed by centrifugation). At Hg concentrations greater than  $5 \times 10^{-4} \text{ M}$ , Hg formed solid metacinnabar particles that were removed from solution by a  $0.1 \text{ } \mu\text{m}$  filter. Organic matter rich in aromatic moieties was preferentially removed with the solid. HPOA, humic and fulvic acids inhibited aggregation to a greater extent 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  $\text{Ca}^{+2}$ . Inhibition of metacinnabar precipitation appears to be the result of strong DOM-HgS interactions. Prevention of aggregation of colloidal particles appears to be caused by adsorption of DOM and electrostatic repulsion similar to the observations made by Horzempa and Helz (12) for covellite ( $\text{CuS}$ ). As was the case in the dissolution experiments, aromatic carbon content of the DOM was an important factor is important in controlling DOM interactions with cinnabar.

## Conclusions

Mercury remains an environmental problem in many ecosystems. This study has provided important fundamental information about the potential role of organic matter interactions by strong complexation and colloidal stabilization relevant to understanding the factors that control the transport and biogeochemical behavior of  $\text{Hg(II)}$  in the Everglades. These reactions are important in many environments and the results obtained in the Everglades are relevant for understanding Hg behavior in other ecosystems.

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