

Interactions Between Dissolved Organic Matter and Mercury

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Effective management strategies for mitigating mercury (Hg) contamination of game fish in South Florida require understanding of the factors and processes resulting in the transport and controlling the reactivity and bioaccumulation of Hg in the Everglades. Our project focuses on the effect of dissolved organic matter (DOM) on the reactivity of Hg in the Everglades. DOM reactivity with Hg is especially important in South Florida because the high production of organic matter in peat soils and wetlands results in large DOM concentrations in surface water and shallow ground water systems in the region. The findings of our project are important to consider in designing remediation strategies. Factors such as vegetation and hydrology, for instance, may be very important in controlling both DOM and Hg reactivity. In addition, our research efforts to study distribution of Hg between DOM and particulate organic matter, and the determination of Hg-DOM binding constants are critical for adequate modeling of Hg in the Everglades.

Our research is driven by the hypothesis that the chemistry and structural characteristics of the DOM in the Everglades strongly influence the processes that control Hg cycling and bioavailability in the environment. Specific ultraviolet absorbance (SUVA) measurements, in combination with DOC and DOC fractionation analyses using XAD resins, were used to determine both the amount and nature of DOC along a north-south transect (approximately 40 miles). Samples collected in the northern part of the transect had higher DOC concentrations, were more aromatic, and had a greater amount of hydrophobic acids and hydrophobic neutrals than samples collected further south. In addition, porewaters were found to contain greater DOC concentrations than overlying surface waters. The porewaters in the eutrophic areas to the north were found to contain the highest DOC concentrations. DOC concentrations and SUVA were lower in those areas with higher concentrations of methylmercury. Our field studies have shown that the amount and nature of DOM in the Everglades is dependent on the dominant vegetation types, hydroperiod, and interactions of surface water with peat porewaters. For instance, in areas where water migrates to the surface through the peat, the DOM was found to be more aromatic and contain greater sulfur content compared to samples where surface water was lost to the subsurface.

The speciation of Hg(II) in aquatic systems depends, in large part, on pH, DOM concentration, the concentrations of inorganic ligands, especially sulfide, and the distribution of Hg(II) between dissolved and particulate phases. The hydrophobic acid fraction (HPOA), hydrophilic acid fraction (HPIA), fulvic acid and humic acid were isolated from surface waters along the transect 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 using an ion-exchange technique designed to yield information on Hg-DOM binding constants. In each of these studies, organic matter from the northern, eutrophic field sites interacted more strongly than did samples from the southern part of the transect. These isolates were more aromatic and contained greater amounts of reduced sulfur than other samples studied.

Cinnabar is a relatively insoluble solid ($\log K_{sp} = -52.4$) under most environmental conditions. 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. In model compound studies, cysteine and thioglycolic acid dissolved small amounts of Hg from the cinnabar surface, while 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 $^{13}\text{C-NMR}$) of the DOM.

Conversely, precipitation and aggregation of metacinnabar (black HgS) was inhibited in the presence of low concentrations (≤ 3 mg C/L) of DOM isolated from the Florida Everglades. At low Hg concentrations ($\leq 5 \times 10^{-8}$ M), DOM completely prevented the precipitation of metacinnabar. Organic matter rich in aromatic moieties was more reactive with colloidal and particulate HgS. 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. The interactions of DOM with HgS in these experiments appear to be the result of strong DOM-Hg binding and colloidal stabilization.

The strength of DOM – Hg binding interactions was investigated using competitive binding on ion-exchange resins. We compared the distribution ratios for mercury between the resin and water ($[Hg_{\text{resin}}]/[Hg_{\text{soln}}]$) 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. 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 with the samples from the northern sites binding most strongly.

Finally, DOM also was found to influence the binding of Hg(II) to two Everglades peat samples. This is significant because it is hypothesized that dissolved Hg is more bioavailable than particulate bound Hg. Again, the HPOA isolate from the northern, eutrophic site was more effective at competing with the peat for Hg(II). Our studies have demonstrated that the chemical composition of the DOM, especially aromatic carbon and reduced sulfur functional group content, is important in controlling DOM interactions with Hg(II). These interactions are important factors controlling both bioavailability and photochemical reactivity of Hg in the Everglades.