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# Mercury-Dissolved Organic Carbon Interactions in the Florida Everglades: A Field and Laboratory Investigation

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There is increased awareness of mercury (Hg) contamination of game fish in South Florida. Effective management strategies for dealing with this problem require understanding of processes resulting in occurrence and transport of Hg, and control of its reactivity in the Everglades. Interaction of Hg with dissolved organic carbon (DOC) has been proposed as a mechanism for Hg transport in aquatic systems because of a correlation between dissolved Hg and DOC concentrations in natural waters. Mercury DOC interactions play an important role in controlling the availability of Hg for uptake by living organisms. DOC reactivity is important in South Florida because of its high production in the peat soils, wetlands, and shallow ground-water systems in the region.

The South Florida Water Management District, the U.S. Environmental Protection Agency, and the U.S. Geological Survey South Florida Ecosystems Initiative have organized a collaborative intensive study of surface-water chemistry in southern Florida. In 1994, several onsite research locations were selected in the Water Conservation Areas of the Everglades in conjunction with this multidisciplinary, multiagency research project. Our project goal is to understand the interactions of Hg and DOC to better define this important, albeit, poorly understood process. The hypothesis is that the chemistry and structural characteristics of DOC in the Everglades have a strong influence on the processes that control Hg cycling and bioavailability in the environment.

Research accomplishments summarized here are described in detail on the WEB at [http://wwwbrr.cr.usgs.gov/projects/SW\\_corrosion](http://wwwbrr.cr.usgs.gov/projects/SW_corrosion). Three areas of progress will be summarized here:

1. Field and laboratory analysis of water samples collected in the Everglades: We have completed chemical analysis for samples collected in canals and marsh sites from March 1995 to January 1998 as part of a study to quantify the interaction of DOC with Hg. Results from 11 field trips are based on onsite and laboratory measurements for 758 samples collected at 34 locations. A representative sample data set is available at our project WEB site, [http://wwwbrr.cr.usgs.gov/projects/SW\\_corrosion](http://wwwbrr.cr.usgs.gov/projects/SW_corrosion). The complete data set is available at the South Florida Ecosystem WEB site (<http://fl-water.usgs.gov/exchange/exchange.html>).

Speciation of Hg in aquatic systems depends, in large part, on the pH and concentrations of DOC, sulfide, and dissolved oxygen (DO) in surface water and porewater. Spatial and temporal monitoring of these constituents, which are critical to the understanding of processes controlling Hg bioavailability, were conducted at oligotrophic (nutrient poor) and eutrophic (nutrient rich) sites in the south Florida Everglades. Close-interval vertical measurements of sulfide and DO concentrations were made both on a seasonal and diel timescale using water-quality multiprobes, a DO microprobe, and a portable spectrophotometer. Water samples were also collected for Hg, DOC, sulfate, and chloride determinations.

Oligotrophic and eutrophic sites differ with respect to production and exchange of sulfide and oxygen between the sediments and water column. The diel fluctuations of sulfide appear to be influenced by photosynthesis and availability of sulfate. The oligotrophic site exhibits a positive correlation between methylmercury and sulfide with coincident maximum concentrations near

midnight, indicating a diel response. Although the eutrophic site showed large concentration gradients and diel changes between surface water and porewater for DOC, sulfide, and DO, Hg showed no diel change.

2. Laboratory studies of DOC isolated from the Everglades: Organic matter isolated from the Florida Everglades caused a dramatic increase in Hg release from cinnabar (HgS) under most environmental conditions. Hydrophobic (humic and fulvic) acids dissolved more Hg than hydrophilic acids and other nonacid fractions of DOC. HgS dissolution was inhibited by divalent cations such as calcium ion, but was independent of oxygen content in experimental solutions. The presence of various inorganic (chloride, sulfate, or sulfide) and organic ligands (salicylic acid, acetic acid, EDTA, or cysteine) did not enhance the dissolution of Hg from HgS.

Precipitation and aggregation of metacinnabar (black HgS) was inhibited in the presence of low concentrations of DOC isolated from the Florida Everglades. At low Hg concentrations ( $\leq 5 \times 10^{-8}$  M), DOC prevented the formation of metacinnabar. At moderate Hg concentrations ( $5 \times 10^{-5}$  M), DOC inhibited the aggregation of colloidal metacinnabar. At Hg concentrations  $> 5 \times 10^{-4}$  M, metacinnabar precipitated in the presence of organic matter and was removed from solution by filtration with a 0.1 m filter. In this precipitation reaction, organic matter rich in aromatic moieties was preferentially removed with the solid. Hydrophobic acids inhibited precipitation better than hydrophilic acids. Calcium favored metacinnabar formation even in the presence of DOC, but the magnitude of the effect was dependent on the concentrations of DOC, Hg, and calcium ion. Inhibition of precipitation appears to be a result of strong DOC-Hg binding and prevention of aggregation of colloidal particles through surface interactions.

An ion-exchange distribution method was used to determine the stability constants of Hg complexed by DOC isolated from the Everglades. For comparison, the stability constants of several inorganic (chloride, bromide) and organic ligands (citric acid, thioglycolic acid) were also determined by this method. At fixed pH (6.0) and equal ligand concentrations ( $2 \times 10^{-4}$  M), the distribution ratio ( $[Hg_{resin}]/[Hg_{solution}]$ ) in the presence of DOC was comparable to the values for strongly binding ligands such as thioglycolic acid ( $\beta_{HgL} = 10^{30}$ ). Experimental constants for Hg-DOC interaction were  $10^{10.3}$  to  $10^{11.2}$ . Differences between the expected and experimental values for model ligands (and by analogy for DOC) were attributed to the limitations of the ionexchange method.

3. Hg-DOC speciation and modeling studies: The computer ionic speciation model "WHAM" (Windermere Humic Aqueous Model) was used to characterize the Hg-organic species present in Everglades surface water. WHAM focuses on hydrophobic acid-metal interactions. These calculations indicate that the major Hg species in solution change from uncharged chloro- and hydroxycomplexes to charged DOC-bound complexes in the presence of high DOC concentrations ( $< 10$  mg/L C). Inorganic speciation calculated using WHAM has been compared to speciation determined with PHREEQC (pH-redox-equilibrium-equations) with good agreement. WHAM has also been satisfactorily tested using laboratory measurements of calcium ion binding to a soil fulvic acid. Sulfide and sulfur containing ligands shift Hg speciation to Hg-sulfur and Hg-organosulfur complexes. Examination of Hg sulfide and Hg thiol binding constants suggests that sulfhydryl groups may preferentially bind Hg in competition with sulfide ion.

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By Sarah Gerould and Aaron Higer, Compilers

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