

## INTERACTIONS OF MERCURY WITH DISSOLVED ORGANIC CARBON IN THE FLORIDA EVERGLADES

There has been increased awareness by both public and scientific communities over mercury contamination of game fish in South Florida. Effective management strategies for dealing with this problem will require a more thorough understanding of the factors and processes that result in the generation and transport of mercury, and control its reactivity in the Everglades. The role of mercury complexation by dissolved organic carbon (DOC) has been proposed by several investigators as a primary mechanism for the transport of mercury in aquatic systems. However, this relationship has been simply proposed based on a strong correlation between dissolved mercury and DOC concentrations in ground, lake and stream waters. Interactions with DOC may be an important process for controlling the transport and bioavailability of mercury.

The issue of carbon reactivity in South Florida is especially relevant due to the high natural production of organic carbon in the peat soils and wetlands, the relatively high carbon content of shallow ground water systems in the region, the interactions of organic matter with mercury, other trace metals, and anthropogenic compounds, accumulation of organic carbon in corals and carbonate precipitates, and the potential changes in the quality and reactivity of dissolved organic carbon (DOC) resulting from land use practices. This study will attempt to meet the need to more clearly understand the dynamics of organic matter mercury interactions in the Florida Everglades by focusing research on the effect of dissolved organic carbon (DOC) on the transport and reactivity of Hg in the Everglades.

### PROJECT GOAL

It is well recognized that the chemical forms of mercury in the water column and sediments are intimately related to bioaccumulation and body burden. Interactions of mercury and dissolved organic matter may play an important role in controlling the bioavailability and reactivity of mercury. The goal of our research is to provide information

about the interactions of mercury and dissolved organic matter that will better define this important, albeit, poorly understood process. Ultimately, this research will lead to a more complete model of mercury behavior in the Everglades. Our research will focus on the effect of DOC on the transport and reactivity of mercury in the Everglades through a combined field and laboratory study. The underlying hypothesis of this research is that the chemistry and structural characteristics of organic matter in the Everglades have a controlling influence on mercury cycling processes such as methylation and volatilization.

### BACKGROUND

Organic matter in aqueous systems is an important chemical constituent that is important for a number of chemical and biological processes. Organic matter often controls geochemical processes by acting as pH buffers, by affecting the transport and degradation of pollutants, and by participating in mineral dissolution/precipitation reactions. Dissolved and particulate organic carbon may also play an important role in the ecology of aquatic systems by controlling the depth of the photic zone in surface waters, by influencing the availability of nutrients and by serving as a carbon substrate for microbially mediated reactions.

The organic carbon story begins with microbial degradation of plant material and organic detritus by bacteria, fungi and other organisms. These biological processes result in the formation of many of the compounds that comprise the organic matter found in soils, peat, and aquatic systems. Organic matter derived from different source materials has distinctive chemical characteristics associated with those materials. These differences in chemical nature control the reactivity of the organic matter. Once in the system, organic compounds, whether they be man-made or naturally derived, can be truly dissolved, associated with immobile particles or associated with mobile particles (DOC, colloids). Each species



Map of South Florida showing the study area (darkened)

is interrelated to other chemical components in the system, such as mercury.

Most of the dissolved organic matter in the Everglades originates from the degradation and leaching of organic detritus resulting from the algae, bacteria and macrophytes living within the wetland environment. In addition, organic matter is also transported to the Water Conservation Areas of the Everglades in the canals that drain the Everglades Agricultural Area. The ecological and chemical significance of the organic matter at a given place is determined by its chemical nature - not all organic compounds react in the same way or to the same degree.

### WHAT ARE THE KEY ISSUES FOR THE EVERGLADES?

#### *DOC-Mercury Interactions*

The role of mercury complexation by DOC has been proposed by several investigators as a primary mechanism for the transport of mercury in aquatic systems. However, this relationship has been simply proposed based on a strong correlation between dissolved mercury and DOC concentrations in ground, lake and stream waters. The vast majority of mercury in aquatic systems resides in organic-rich soils and sediments. Interactions with DOC, however, may be an important process for the release of mercury into

porewaters with subsequent transport into surface waters. Effective management strategies for dealing with this problem will require a more thorough understanding of the factors and processes that result in the generation and transport of Hg, and control its reactivity in the Everglades. Our studies will focus on the effect of dissolved organic carbon (DOC) on the transport and reactivity of Hg in the Everglades.

#### *Effects of land use practices*

Land and water use practices can result in changes in the quality, quantity, and reactivity of DOC. Agricultural practices, for instance, result in the removal of native sources of DOC and the addition of anthropogenic compounds in the form of herbicides, pesticides and surfactants. The DOC resulting from these practices is, therefore, different in nature from the original DOC of the region. In addition, the hydrologic condition of the wetlands themselves will also impact both the quantity and reactivity of the DOC moving through the system. For instance, water table changes can markedly change DOC by introducing oxygen into the unsaturated zone. USGS research is attempting to determine the effect of land and water use practices on the quantity and nature of the bulk DOC in the South Florida system. The first objective is to demonstrate that these practices have a significant effect on the nature of the DOC thereby affecting the chemical properties of the DOC. The second objective is to demonstrate that DOC interactions within a given environment determine the behavior of mercury in the system.

#### **PLAN OF STUDY:**

This project will use a combined field/laboratory approach to assess the significance and strength of DOC-Hg interactions in the Everglades. Both the inorganic composition and organic matter associated with surface water, pore waters, and ground water from the Everglades will be characterized. Temporal variations in mercury and DOC concentrations will be measured at appropriate sampling locations to provide a measure of the mercury and DOC loadings in the system. These measurements will be coupled with determinations of the nature of the DOC

inputs under different hydrologic conditions (low and high flow conditions). Major fractions of the DOC, such as aquatic humic substances, will be isolated from the water samples and characterized by determining elemental composition, molecular weight, functional group content and structural characteristics.

The isolates and whole water samples will be used to study interactions of DOC with mercury in laboratory experiments using both radio-labeled ( $^{203}\text{Hg}$ ) and non-labeled mercury under a range of pH and concentration conditions. In addition, these measurements will also be made with previously isolated samples that vary significantly in structural composition. The goal of these measurements will be to provide distribution coefficients for relevant mercury species with aquatic humic substances and DOC, in general. These coefficients will then be correlated with the structural properties of the organic matter to provide inexpensive analytical parameters to be used to estimate the strength of DOC-mercury interactions in the Everglades.

Finally, using the binding constants determined in the laboratory studies, a computer program will be used to model the geochemical behavior of mercury in the Everglades. This model will allow us to synthesize the overall effects of the DOC-Hg associations and how they change as the qualitative and quantitative character of the DOC varies in our study systems.

#### *Anticipated Schedule:*

March 1995: Begin seasonal field sampling and sample analyses at select sites within the study area.  
January 1996: Begin compiling water quality data as a USGS Open File report for ongoing field work.  
July 1996: Continue field sampling. Begin characterizing organic matter isolates and measuring DOC-Hg binding constants.  
January 1997: Continue field sampling. Compile report on characteristics of DOC in the Everglades. Continue determination of Hg binding constants.  
January 1998: Compile report on Hg binding constants.

#### *Planned Products:*

- USGS Open File report series of water quality data.
- Journal articles detailing the spatial, seasonal and hydrologic variability in DOC.
- PhD thesis and journal articles describing DOC-Hg binding constants

#### **COLLABORATORS:**

Data collection for this project requires the collaboration of scientists from the USGS (Reston, Madison and Menlo Park), from the Wisconsin Department of Natural Resources, the Benedict Estuarine Laboratory, Academy of Natural Sciences of Philadelphia, and the South Florida Water Management District. Binding constants will be determined in collaboration with scientists from the USGS (Madison) and the University of Colorado, Boulder, Colorado. Chemical modeling will be done in collaboration with the US EPA, Athens, Georgia.

#### **BENEFITS:**

- Detailed understanding of the influence of hydrologic and seasonal factors on the variation in the nature and amount of DOC and mercury in the Florida Everglades.
- Distribution coefficients for mercury with dissolved organic carbon and aquatic humic substances that are currently unavailable.
- The identification of easily determined analytical parameters that can be used to predict potential organic matter-mercury interactions.
- Incorporation of organic matter properties and distribution coefficient data for mercury into a speciation model to more adequately determine speciation of mercury in aquatic systems, and to provide predictive capabilities for the behavior of mercury in other aquatic systems.

#### **FOR MORE INFORMATION:**

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