

# Mercury Studies in the Florida Everglades



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## Background

Public concern for wildlife and human health problems due to mercury (Hg) toxicity has increased substantially since the mid-1980's. These concerns are manifested primarily by the issuance of fish consumption advisories in the majority of U.S. states, Canada, and several European countries because of high levels of mercury in game fish. Although the precise causes for this contamination problem are not completely understood, it appears that there are both source and ecosystem-specific factors that can result in elevated levels of mercury in game fish. Because mercury is known to adversely affect the human brain and nervous system, health concerns arise when elevated concentrations of mercury are detected in game fish from ecosystems where there is subsistence level consumption of fish. In extreme cases such as the Everglades, where mercury concentrations in fish consistently exceed the Florida advisory level of 1.5 parts per million, even occasional fish consumption is not recommended.

For most aquatic ecosystems, atmospheric deposition is the primary source of mercury, although there are numerous instances of geologic and anthropogenic point-source contamination. There are many sources of mercury to the atmosphere, both natural and human related. Natural sources include outgassing from the oceans, volcanoes, and natural mercury deposits. Coal combustion, waste incineration, chloralkali production, and metal processing are the dominant human-related sources to the atmosphere. In ecosystems for which atmospheric deposition is the dominant source, resulting concentrations of total mercury in water are very low, generally less than 10 nanograms per liter (ng/L). The challenge to scientists is to explain the series of processes that lead to toxic or near-toxic levels of mercury in organisms near the top of the food chain (bioaccumulation), when aqueous concentrations and source-delivery rates are so low. To understand this phenomenon adequately, scientists must apply an interdisciplinary approach wherein various components of an ecosystem (atmosphere, biota, surface water, ground water, and sediments) are studied contemporaneously. The purpose of this fact sheet is to describe the mercury contamination problem in south Florida, and the interdisciplinary project that was assembled under the auspices

of the U.S. Geological Survey South Florida Ecosystem Program to investigate the underlying processes that cause mercury bioaccumulation.

## Mercury in the Geochemical Cycle and Food Chain of the Everglades

The fate of mercury in the Everglades ecosystem is controlled by the geochemical cycle and food-chain transfer steps (fig. 1). Although most mercury is likely derived from atmospheric deposition, other potential mercury sources exist, such as ground-water discharge and water from drainage canals. The dominant form of mercury in atmospheric deposition is ionic mercury [Hg(II)], but once in surface water of an aquatic ecosystem, rapid geochemical transformations can occur. The transformation of Hg(II) to methylmercury [CH<sub>3</sub>Hg<sup>+</sup>]

is referred to as methylation. From a toxicity perspective, methylation is an important step, because CH<sub>3</sub>Hg<sup>+</sup> is the most bioaccumulative form of mercury and comprises almost all the mercury in consumable fish. Although several biological and non-biological processes can methylate mercury, scientists generally agree that methylation by sulfate-reducing bacteria is most important. This process is localized where the bacteria concentrate, such as at the sediment/water interface or in algal mats. Demethylation also occurs, which is the process of transforming CH<sub>3</sub>Hg<sup>+</sup> to Hg(II) or to elemental mercury [Hg<sup>0</sup>]. This is an important process because the mercury byproducts of this process are less bioaccumulative and Hg<sup>0</sup> is removed from the water surface by transfer to the air (evasion). Dissolved organic carbon (DOC) in Everglades water is not only responsible for its characteristic brown color, but also is an important transport vehicle for mercury.

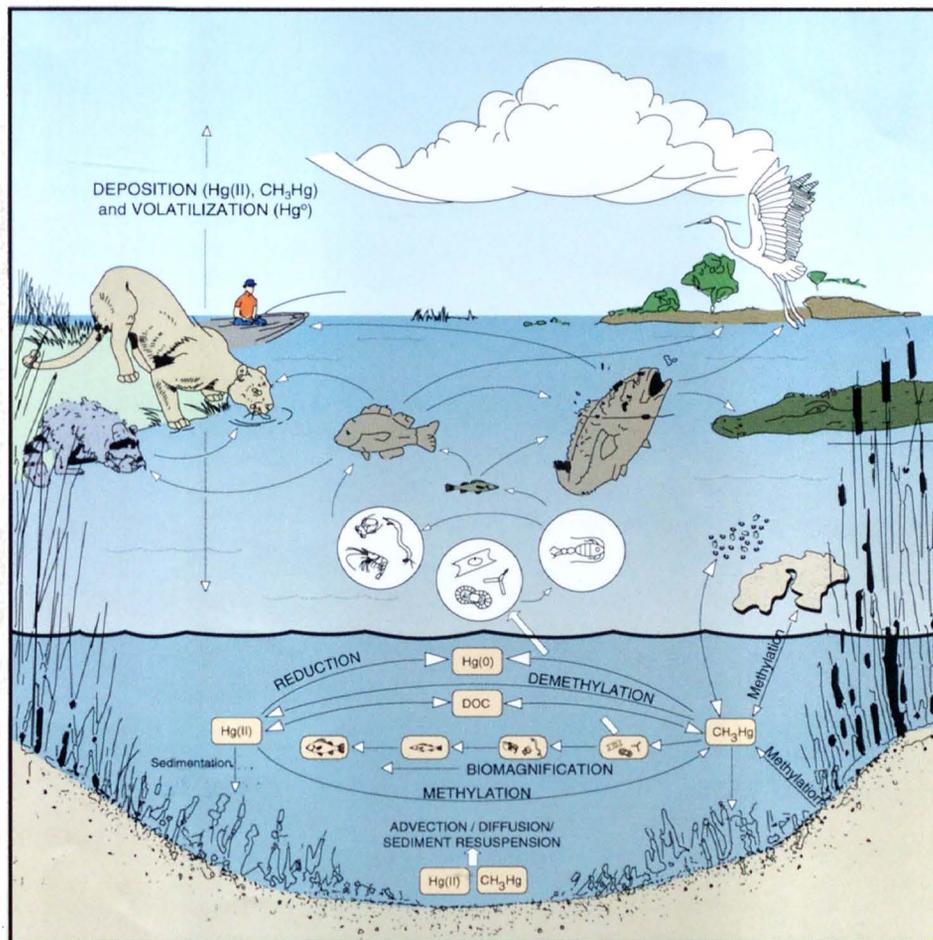


Figure 1. Schematic representation of the mercury geochemical cycle and the pathways of mercury through the food chain in the Florida Everglades.

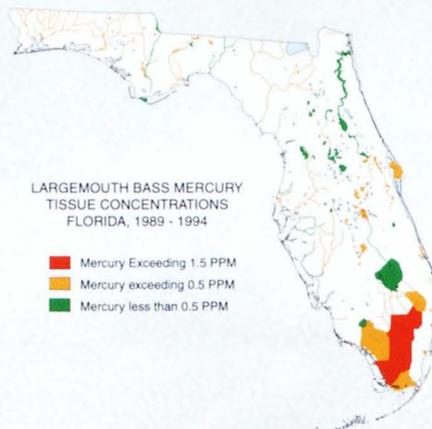
Mercury associates with DOC in water and generally increases the concentration of mercury that can be maintained in water. Depending on local conditions, DOC-Hg binding can either increase or reduce mercury uptake by organisms. If DOC-Hg bound mercury is transported to a site where methylation is occurring, enhanced toxicity results; however, if DOC-Hg binding is strong enough, DOC can limit the availability of mercury for methylation.

The precise mechanism for transfer of  $CH_3Hg^+$  to the food chain is unknown, but likely involves the consumption of methylmercury-containing bacteria by the next higher level in the food chain (likely plankton) or direct adsorption of  $CH_3Hg^+$  dissolved in water. The initial food chain transfer step is vitally important, because concentrations of mercury in plankton increase about ten thousand fold over water concentrations. This process is called biomagnification. Because organisms cannot eliminate mercury as fast as it can be ingested, mercury tends to accumulate as one proceeds up each remaining food-chain level. However, the bio-magnification factor between each of these levels is about ten fold or less. Although the transfer routes and controlling processes of mercury in the food chain are generally known, many complicating factors make food-chain studies difficult, including: precise knowledge of what certain organisms consume, seasonal presence/absence of prey, and the fact that mercury concentrations generally correlate with the age of an organism.

### Is mercury contamination in the Everglades different than elsewhere, and if so, why?

Mercury concentrations in game fish from in the Everglades region are some of the highest observed anywhere in the world. A state-wide sampling of Largemouth Bass in the late 1980's revealed that the fish in one-half to two-thirds of Florida's lakes contained elevated levels of mercury (fig. 2). Many of the lakes and streams across northern and central Florida were found to have Largemouth Bass with average mercury concentrations between 0.5 and 1.5 parts per million (ppm), which is cause for issuing a limited consumption advisory for the general population; with even more stringent recommendations for women of child-bearing age, and children. A much more severe problem was revealed in the Everglades, however, where nearly a million acres of this ecosystem was found to have average mercury concentrations in Largemouth Bass exceeding 1.5 ppm, resulting in a "do not consume advisory" for this region.

The severe mercury problem in the Everglades is likely the result of naturally occurring



**Figure 2.** Mercury concentrations in Largemouth Bass in Florida. (Source: F.J. Ware, H. Royals, and T. Lange, 1990, Proceedings of the Annual Conference of the Southeastern Association of Fish and Wildlife Agencies, v. 44, p. 5–12).

conditions that make the ecosystem prone to mercury methylation and bioaccumulation, and the exacerbating effects of many disturbances caused by a large, nearby human population. Most wetland systems, like the Everglades, have the necessary ingredients that tend to promote elevated levels of  $CH_3Hg^+$  in organisms, such as ample DOC, organic substrate (peat), and low to neutral pH. In addition, relatively high sulfate levels and a subtropical climate in the Everglades region provide optimal conditions for sulfate-reducing bacteria to methylate mercury. The human effect on the mercury problem in the Everglades centers on three issues: (1) Hg-containing emissions from incinerators and power generating utilities; (2) increased soil-mercury mobilization promoted by drainage and soil disturbance in the Everglades Agricultural Area (EAA); and (3) hydrologic changes resulting from the Central and South Florida Flood Control Project.

### The USGS South Florida Ecosystem Program

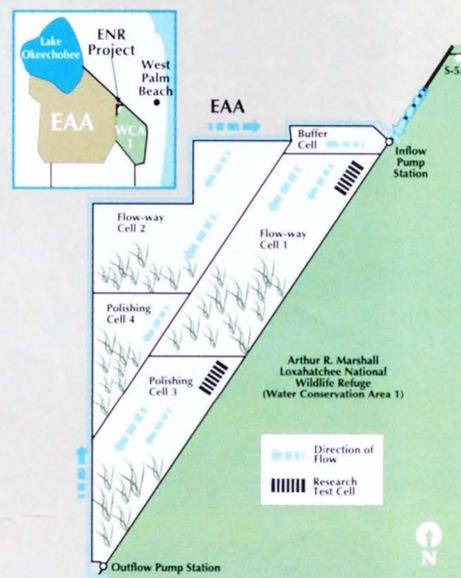
The USGS South Florida Ecosystem Program is part of an intergovernmental effort to restore and maintain the ecosystem of south Florida. One element of the restoration effort is the development of a scientific basis for resource management decisions. Mercury contamination in the Everglades has been identified by local, state, and national agencies as a topic of great concern, and in need of research to provide the information to base restoration plans. The South Florida Water Management District (SFWMD), Florida Department of Environmental Protection (FDEP), U.S. Environmental Protection Agency (USEPA), and the National Marine Fisheries Service need information on mercury cycling to predict the effects of proposed restoration plans on mercury exposure. The Everglades Forever Act of

1994 has mandated management decisions regarding what can be done to mitigate the toxic effects of mercury in the Everglades.

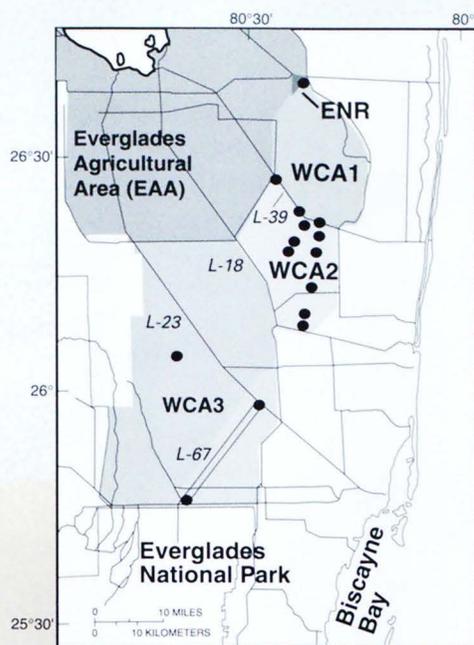
### Mercury Cycling in the Florida Everglades Project

In response to this request from resource managers for more scientific information on mercury cycling in the Everglades, the USGS South Florida Ecosystem Program, SFWMD, and USEPA are co-funding a group of scientists to study mercury bioaccumulation in the Everglades. Participating scientists are from several agencies, including: USGS, SFWMD, FDEP, USEPA, Wisconsin Department of Natural Resources, and University of Wisconsin-Madison. The overall objective of this project is to provide resource managers scientific information on the hydrologic, biologic, and geochemical processes controlling mercury cycling in the Everglades. It is anticipated, however, that information from this project will be transferrable to other ecosystems where mercury problems arise. Specific areas of research among the group includes: geochemical studies of mercury, mercury methylation and demethylation studies, DOC-Hg interactions, mercury accumulation in sediments, diagenetic processes in peat, sulfur cycling studies, biological uptake of mercury and lower food chain transfer pathways, and groundwater/surface-water exchange.

From a resource management perspective, one of the primary concerns of this project is the long- and short-term effects of the Everglades Nutrient Removal (ENR) project (fig. 3), which is a crucial component of the



**Figure 3.** Schematic diagram of the Everglades Nutrient Removal Project showing location of the project, direction of flow, and spatial arrangement of the pump stations, test cells, and interior levees.



**Figure 4.** Location of the sampling stations for the Mercury Cycling in the Everglades project from March 1995 through June 1996. The satellite image shows the effects of phosphorous-rich water draining from the EAA into the L-39 canal, and then into WCA2, where cattails (green area emerging from the canal) are replacing sawgrass as the dominant vegetation.



SFWMD's restoration plans. The ENR project calls for the construction of stormwater treatment areas (STAs), which are reclaimed agricultural lands that will be permanently flooded with water draining from the EAA and thus reduce phosphorus loads to the Water Conservation Areas (WCAs) by sequestering phosphorus through biological uptake. Questions have arisen concerning whether enhanced mercury methylation might result within the STAs and present a toxicological hazard for wildlife residing there, or whether potentially high levels of  $\text{CH}_3\text{Hg}^+$  in outflows from the STAs might present an environmental hazard to wildlife in the WCAs.

Initially, this project is focusing on field sites in the northern Everglades (fig. 4), where phosphorus loading from the EAA and its impact on mercury cycling is of concern. Sampling stations include several sites within the ENR, canals, and marshes. Sites along the L-39 canal were chosen to examine how mercury levels change with distance from the EAA and as water leaves the canals through levee spillways and encounters more quiescent conditions of WCA2. Sites within WCA2 are along a transect that spans the region of greatest phosphorus impact (as indicated in the satellite image map, fig. 4) to the middle of WCA2 and WCA3 where more natural phosphorus conditions prevail. The two sites along the L-67 canal were chosen because this area showed the greatest Hg concentrations in largemouth bass.

The following are brief descriptions of each of the subprojects that make up the "Mercury Cycling in the Everglades" project.

### **Geochemical Process Studies of Mercury**

To understand how mercury is transported and transformed in the environment, a basic understanding of the spatial occurrence and predominance of the forms of mercury is necessary. Mercury concentrations in water are so low, however, that samples collected for this part of the project require the use of ultra-clean techniques (fig. 5). Specific study objectives for this aspect of the project include: (1) determination of spatial variability and predominance of the specific forms of mercury in water and suspended particles; (2) investigation of the factors controlling the short-term varia-



**Figure 5.** Scientists collecting water samples for mercury analysis need to adhere to strict, ultra-clean sampling protocols, which include the use of nonmetallic lint-free suits, plastic gloves, and stringently cleaned sample containers.

tions in mercury transformation processes; (3) examination of factors controlling the spatial and temporal variability of mercury methylation; and (4) determination of the important locations and mechanisms of food-chain uptake of mercury.

### **Methylmercury Degradation Studies**

Because methylmercury is the most bioaccumulative form of mercury and thus the most toxic, it is important to understand what controls the detoxification process of demethylation. Scientists currently hold that demethylation can proceed along two pathways: methyl-cleavage and oxidative demethylation. The objective of this study is to understand the environmental factors regulating these two processes.

### **Dissolved Organic Carbon-Hg Interactions**

By effectively binding mercury, DOC provides a mechanism to mobilize mercury and many other trace metals in the environment which would otherwise be virtually immobile. This project seeks to: (1) identify the origin(s) of the DOC in the Everglades system; (2) define how the quantity and quality (molecular makeup) of DOC changes throughout the system; (3) determine what controls the reactivity (binding) of mercury with DOC, and how it varies across the ecosystem; and (4) understand how land use and hydrologic changes affect DOC.

### **Sulfur Cycling Studies**

Mercury transport, accumulation, and cycling are controlled by several microbially mediated processes, many of which are related to sulfur cycling. Although it is now known that sulfate reducing bacteria are the principal organisms responsible for mercury methylation in the Everglades, the relation between sulfur cycling and mercury methylation is not well understood in general. The objective of this study is to relate sulfur reactions and isotopic composition and their relation to changes in nutrient concentrations, season, rates of sedimentary deposition, and ultimately to mercury cycling.

### **Mercury Accumulation and Diagenetic Processes in Peat**

Like most wetlands, the Everglades has an accumulation of surficial peat. Because mercury has a strong affinity for organic matter, mercury that has accumulated in the peat represents the vast majority of what is found in the entire ecosystem. Peat deposits, however, are also known to be areas of significant physical and chemical change (diagenesis). Many biogeochemical pro-

cesses that control the mobility of most nutrients and trace metals, including mercury, operate in peat. Therefore, it is important to understanding the processes that result in mercury accumulation and potential remobilization in peat. The objectives of this study are to determine the size of the mercury reservoir within the peat, ascertain how diagenetic processes may be affecting the stability of this reservoir, and document historical changes in mercury accumulation rates in the peat.

### Biological Uptake of Mercury and Lower Food Chain Transfer Pathways

The assemblage of microalgae that live on shallow submerged substrates are referred to collectively as periphyton. This periphyton covers most submerged plants and forms a thick mat on the sediment surface in many locations in the Everglades. In this ecosystem, periphyton growth is responsible for the majority of primary production, and thus is an important food source. The linkages between the primary producers (periphyton), primary consumers (invertebrate organisms consuming and living in and around the periphyton) and secondary consumers (predaceous fish) are important to document to fully understand how the bioaccumulation process operates in the Everglades. The objectives of this study are to: (1) determine whether mercury methylation is actively occurring in the periphyton, and if so, is this mercury being transferred to the food chain, and (2) document the important food chain linkages of mercury

transfer from the primary producers to predaceous fish.

### Ground-Water/Surface-Water Exchange

One potentially important source of mercury to the Everglades, yet currently not quantified, is ground-water discharge. Ground water also contains other important ingredients for the methylation process, such as sulfate and DOC. To date, however, very few studies have examined the nature of ground-water/surface-water exchange in the Everglades. The specific objectives of this study are to: (1) determine water fluxes and hydraulic properties of sites in the ENR and WCA2; (2) relate those fluxes to hydrogeologic properties, climatic variability, and water-level management strategies; and (3) estimate ground-water fluxes of mercury and nutrients to surface water.



Many parts of the Everglades are very difficult to get to, so scientists use helicopters and airboats to expedite sampling and to ensure that sample integrity is not jeopardized by extended holding times.



Periphyton mats are widespread across the Everglades. Studies are being conducted to determine the role of periphyton in the mercury cycle, including whether it represents a mercury introduction point to the food chain.



What was once a natural flowage from Lake Okeechobee to the discharge point of the Shark River Slough, the Everglades is now one of the most hydrologically managed ecosystems anywhere. Water levels are managed throughout the Everglades by some of the largest pumping stations in the world and an intricate system of canals to meet human-use and ecosystem needs.

### Anticipated Project Schedule:

March 1995: Begin sampling in northern Everglades Sites (ENR, L-39 canal, WCA2)

July–December 1995: Continue sampling northern everglades sites, and add sites in L-67 canal and WCA3. Initiate intensive, short-term sampling in WCA2.

March–June 1996: Continue sampling at established sites. Publish data on World Wide Web (WWW) and write manuscripts for scientific journal publication.

October 1996–September 1997: Continue sampling, and add more southern sites in WCA3 and Taylor Slough. Write up annual reports and keep WWW database current.

October 1997–September 1998: Continue sampling southern Everglades sites and add sites in Big Cypress National Preserve.

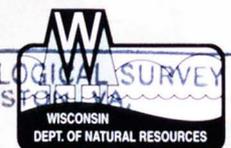
October 1998–September 1999: Write synthesis papers on basis of project results.

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