

## Mercury cycling in the Florida Everglades: a mechanistic field study

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### Introduction

Public concern for wildlife and human health resulting from mercury (Hg) toxicity has increased substantially since the mid-1980s. In the Florida Everglades, Hg concentrations in excess of 1.5 mg g<sup>-1</sup> (wet weight) in predator fish have been observed and advisories have been issued for human consumption of all fish. Furthermore, elevated Hg levels have been identified as a principal factor in the death of at least one Florida panther which had a liver mercury concentration of 110 mg g<sup>-1</sup> (JORDAN 1990), and is strongly implicated in the deaths of two other panthers (ROELKE et al. 1991). Restoration plans for the Everglades are nearing completion, and efforts to restore more natural conditions will be forthcoming. State of Florida and federal agencies need to know if changes resulting from these restoration activities will exacerbate or mitigate the mercury problem in the Everglades.

Mercury research projects in the Everglades have been focused on quantifying and identifying sources of Hg and evaluating spatial and temporal distributions in water, sediment, and biota. The Florida Atmospheric Mercury Study (GUENTZEL et al. 1995)

has shown that atmospheric inputs are the dominant input mechanism for Hg to the Everglades. More recently, the South Florida Atmospheric Mercury Study has attributed elevated Hg concentrations in several Everglades rain event samples to local sources (DVONCH et al. 1995). Within the Everglades, the U.S.E.P.A.'s Regional Environmental Assessment and Monitoring (REMAP) study has revealed ecosystem-wide trends in mercury and methylmercury in water, sediments and forage fish (*Gambusia*) (STOBER et al. 1995).

In 1995, the U.S. Geological Survey initiated the ACME project. The overall objective of the ACME project is to conduct intensive, process-oriented research that focuses on the primary mercury cycling pathways in the Everglades. A goal of this research is to incorporate the process-rate finding into a numerical model that can be used for predictive purposes and as a management tool for formulating restoration plans that may help mitigate mercury impacts to this fragile ecosystem. ACME's participating agencies and related study areas are presented in Table 1.

Table 1. Participants and discipline topics for the ACME Project.

Discipline Topic	Group <sup>1</sup>
Aqueous Hg cycling in the water column	USGS-WI, WDNR, UW
Sediments/Pore water	USGS-WI, WDNR, UW
Bioaccumulation	UW, FGFWFC, USGS-CA
DOC-Hg Interactions	USGS-CO, WDNR, UW
Hg Methylation in Sediments and Periphyton	ANS-ERC, UW
Hg Demethylation in Sediments and Periphyton	USGS-CA
Sediment Diagenesis and Sulfur Cycling	USGS-VA
Hg Modeling	TTI

<sup>1</sup>Abbreviations: USGS-WI – U.S. Geological Survey, Middleton, WI; WDNR – Wisconsin Department of Natural Resources, Monona, WI; UW – University of Wisconsin Water Chemistry Program; FGFWFC – Florida Game and Fresh Water Fish Commission; USGS-CA – U.S. Geological Survey, Menlo Park, CA; USGS-CO – U.S. Geological Survey, Boulder, CO; ANS-ERC – The Academy of Natural Sciences Estuarine Research Center; USGS-VA – U.S. Geological Survey, Reston, VA; TTI – Tetra Tech, Inc., Oakville, Ontario.

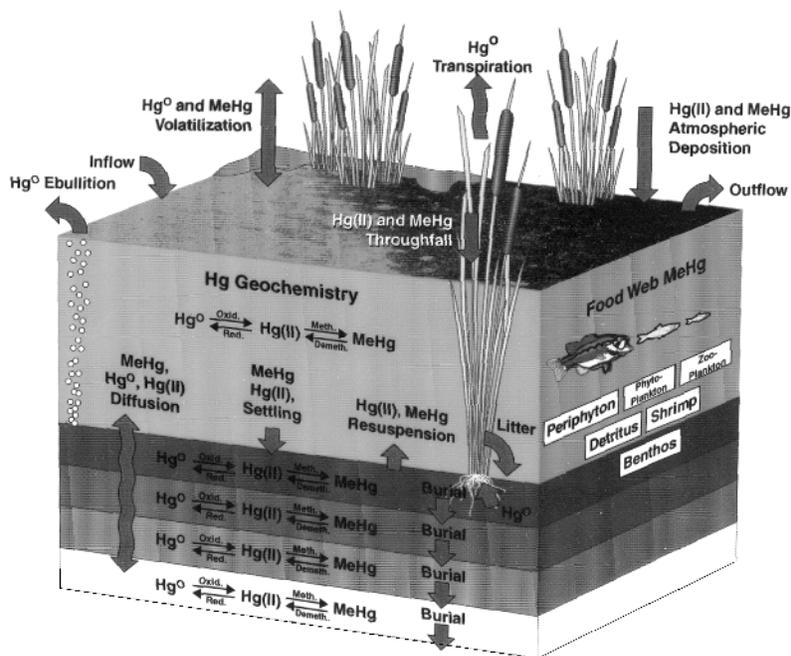


Fig. 1. Conceptual model of the mercury cycle in the Everglades from the ACME project. The model highlights linked sub-models for mercury transport, biogeochemistry, and bioaccumulation.

### Conceptual model of Hg cycling in the Everglades

The ACME project team has formulated a conceptual model of the Hg cycle in the marshes of the Everglades (Fig. 1). The overall model, as well as our project work plan, is based on a linked biogeochemical and food web bioaccumulation approach. Individual participants focus their efforts on particular aspects of the conceptual model, but emphasis is placed on group field efforts to ensure comparability and compatibility of our results. The determination of process rates, or data to allow calculation of process rates that can be used and synthesized by a numerical, mercury-cycling model, are the primary objectives of each participating research groups.

### Results and discussion

The ACME project has made several key contributions toward improving our understanding of the Hg cycle in the Everglades. Many of these contributions are novel and have redefined many paradigms of how the scientific community views the processes controlling

mercury cycling in wetlands, and more generally in the environment. Several major findings of the ACME project are summarized here.

Analysis of aqueous samples for total Hg ( $Hg_T$ ) and methyl mercury (MeHg) can be severely hampered by matrix effects. Analysis of  $Hg_T$  requires pre-oxidation of water samples by exposure to high-intensity ultraviolet (UV) light, presumably destroying dissolved organic carbon in samples. For MeHg analysis of highly sulfidic water samples (a common occurrence in the northern portions of the Everglades), copper sulfate ( $CuSO_4$ ) must be added to samples prior to distillation to remove the complicating effects of high sulfide (OLSON et al. 1997).

Total Hg ( $Hg_T$ ) in the water column of the Everglade's canals and marshes is generally low (less than  $5 \text{ ng L}^{-1}$ ) (HURLEY et al. 1998). Except during high-flow events when resuspension of sediment occurs,  $Hg_T$  levels in canals are on average about 50% less than that observed in

the marshes (2.07 vs. 3.03 ng L<sup>-1</sup>). In addition, methylmercury concentrations in the marshes are on average twice that of canals (0.28 vs 0.14 ng L<sup>-1</sup>). Appreciable MeHg was only observed in canals during periods of flow stagnation. In the marshes of Water Conservation Areas (WCA) 2 and 3, Hg<sub>T</sub> did not reflect any discernable spatial patterns. In contrast, MeHg levels in the water column showed consistent trends with generally lower levels observed in the eutrophied areas of the Northern Everglades and generally higher concentrations in mid-latitude regions (northern WCA 3A). These observations are consistent with experimental studies conducted by the ACME that showed that excessive sulfide levels, such as those observed in porewaters of the northern Everglades, may inhibit mercury methylation (BENOIT et al. 1999a). In the southernmost parts of the study area (Everglades National Park) MeHg levels in marsh waters were intermediate with our other monitoring sites.

The concentrations of the analytically determined species of Hg can vary on a diel basis in Everglade marshes (KRABBENHOFT et al. 1998). Dissolved gaseous mercury (DGM) concentrations peaked at or near solar noon with production ceasing during dark periods. Diel variability of Hg<sub>T</sub> and reactive Hg (Hg<sub>R</sub>) appear to be controlled by inputs from rainfall and sorption/desorption processes. Methyl Hg also showed a diel trend that was apparently unrelated to the aforementioned factors. Detailed sampling efforts of chemical concentration gradients near the sediment-water interface revealed significant releases of MeHg during dark hours, apparently in response to both redox and biologically facilitated transport processes.

Mercury methylation occurs in the sediments of the marshes of the northern Everglades. Although the percent of Hg<sub>T</sub> as MeHg in sediments was similar to that measured in northern USA lake sediments, methylation rates were 100 to 1000 times higher (GILMOUR et al. 1998). Methylation rates within the marshes increased from north to south with lowest rates of production in the eutrophied regions of northern WCA-2, and were inversely correlated with sulfide levels in pore waters. Sulfide

strongly associates with mercury and apparently has a controlling influence on what fractions of the mercury are available for methylation (BENOIT et al. 1999b.)

Methyl Hg degradation occurs in sediments of the Everglades, and is highest in the near-surface floc layer. Methods for measuring MeHg degradation were greatly improved as a part of this project and allowed rate measurements at or near ambient levels of MeHg. System-wide, MeHg degradation rates follow the trends in Hg methylation, with lowest rates measured in the northern eutrophied areas and highest rates to the south in WCA 3A. Oxidative demethylation is an important pathway in the Everglades, and is carried out by methanogens and sulfate reducing bacteria (MARVIN-DIPASQUALE & OREMLAND 1998).

Accumulation of MeHg in biota of the marshes of the Everglades follows the same general trends observed for MeHg in the water column and sediments. However, the magnitude of MeHg accumulation at a given site varies seasonally and does not always appear to be directly related to concurrent levels of MeHg in water (CLECKNER et al. 1998). Identifying the pathways of MeHg through the foodweb(s) of the Everglades is a primary objective of the ACME project, particularly processes leading to MeHg accumulation in primary producers. Detailed studies of periphyton, an abundant component of biomass in the Everglades, collected from sites spanning across the Everglades showed that periphyton communities that support an active microbial sulfur cycle also support mercury methylation (CLECKNER et al. 1999).

Sulfur is an important element in the Hg cycle of the Everglades. Sulfate additions stimulate sulfate-reducing bacteria, which are the primary methylators of Hg in the Everglades. Sulfur is accumulating in sediments of the Everglades (primarily as organic-S) at levels in excess of historical levels. This effect is most pronounced in areas receiving agricultural runoff. In areas where high surface water sulfate levels are observed, high levels of porewater sulfide result, and appear to have a limiting effect on mercury methylation. Sulfur isotopes (<sup>34</sup>S)

are effective tools for tracing sulfur related to agricultural runoff, however, deep groundwater discharge cannot be eliminated as a possible source with the current data set (BATES et al. 1998).

Hydrophobic acids contained in dissolved organic carbon (DOC) from the Everglades significantly increases the overall solubility, and thus the mobility of mercury (RAVICHANDRAN et al. 1998). Proposed mechanisms for this phenomenon include surface complexation or oxidation of surface sulfur species by dissolved organic matter. Thermodynamic calculations suggest that in oxic surface waters DOC is the primary ligand of Hg, whereas in anoxic pore-waters inorganic sulfide is more important (RAVICHANDRAN et al. 1998, BENOIT et al. 1999b).

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