MERGENCY IN THE EVERGLADES ECOSYSTEM

INTRODUCTION

Beginning with detection of elevated levels of mercury in largemouth bass in 1989 (FSU 1990; Ware et al. 1990), it has become increasingly apparent that the South Florida Ecosystem is extensively contaminated. In response to continuing accretion of reports of significant Hg contamination, the State of Florida has issued human health advisories that ban or restrict consumption of freshwater fishes from over 2 million acres of the Everglades and Big Cypress Swamp. Although Hg contamination has been detected at levels of concern in largemouth bass throughout the State (Lange et al. 1993), maximum concentrations found in Everglades largemouth bass (4.4 mg/kg) and bowfin (>7 mg/kg) are the highest Hg contaminant levels thus far reported from Florida waters. Mercury accumulation through the food chain may reduce the breeding success of wading birds (Frederick and Spalding 1994) and the viability of the endangered Florida panther (Roelke et al. 1991).

The sources, distribution, and pathways of transport and transformation of Hg through the South Florida Ecosystem are not well understood. Mercury has been sequestered in the oligotrophic circumneutral Everglades peats through the 5,000-year period of their development. Subsidence of these soils following drainage and enhancement of their nutrient status during agricultural conversion may be mobilizing this geochemical reservoir. The natural Everglades soils were not strongly anaerobic, even though flooded for much of the year (Bachoon and Jones 1992), and increasing anaerobiosis may lead to increases in the importance of organic Hg species in Hg biogeochemical cycles. The 1400 miles of canals now in the system, with their low oxygen content, may provide a primary locale for methylation of Hg and its transport through the system in association with dissolved and finely divided organic matter. Potentially significant external sources include atmospheric deposition from the global and regional background and deposition from more local fossil-fuel electric power plants, garbage incinerators, paints, medical laboratories, and fossil residues from Hg-containing agricultural chemicals.

BIOLOGICAL TRANSFORMATIONS

Background: The high levels of MeHg accumulating in fish and other fauna of South Florida may result from either increasing inputs of Hg to the system or changing environmental conditions that promote formation and transport of MeHg. Although some abiotic methylation of Hg may occur, the predominant mechanism for formation of MeHg in the environment is microbial (Berman and Bartha 1986). Thus, increases in concentration of the methyl form of the element indicate either
higher available concentrations of inorganic Hg or higher rates of microbial transformation activity, or both.

Although there is little information about distribution and transformations of Hg in wetlands, the problem of elevated Hg in fish has been noted in lakes experiencing point source inputs of Hg, recent impoundments, acid inputs, or combinations thereof (Hakanson et al. 1988; Jackson 1988). Methyl mercury, which constitutes a small fraction of total environmental Hg, is the predominant form of Hg present in contaminated fish (Westöö 1973) and is bioaccumulated at high rates (Boudou and Ribeyre 1985). Methyl mercury, introduced as a point source into Minamata Bay, was also identified as the compound responsible for the widespread human toxicity associated with consumption of local fish in Minamata, Japan, in the late 1960s (D'Itri 1972).

More commonly, however, environmental Hg contamination cannot be attributed to external sources, but rather stems from alterations of environmental conditions that mobilize Hg and promote uptake via methylation. Widespread Hg contamination was identified in lakes in Scandinavia, eastern Canada and the north-central U.S. (Hakanson et al. 1988, Jackson 1988); surveys of affected lakes implicated acidification of poorly buffered lakes and/or recent impoundment as contributing to elevated Hg levels in fish.

The distribution of total Hg in soils and sediments of Everglades (Delfino et al. 1993) indicates an increase in the accumulation rates of Hg for the 90 years since the turn of the century, with pronounced increases dating from 1940. The similarity of these data to trends in lakes of the north-central U.S. and Sweden, despite differences in climate, hydroperiod, vegetation and location, implicates the worldwide increases in Hg inputs accompanying industrialization. However, the distribution of increases in accumulation rates within the Everglades is not uniform; WCA 1 and WCA 2 have the highest increases, implicating either localized sources or internal transport and transformation processes.

There are no historic or present measurements of Hg methylation in the Everglades; thus no direct comparisons of the rates of methylation between the Everglades and other systems, or between present-day and historic rates within the Everglades, can be made. Rather, present and past conditions in the Everglades can be compared with those factors known to control rates of Hg transformations in other surface water systems to formulate hypotheses about current levels of MeHg and its uptake into the food chain.

The net rate of Hg methylation in the environment reflects the relative rates of two microbial processes: methylation and demethylation. Methylation is primarily carried out by sulfate-reducing bacteria in both freshwater and saltwater systems. Although many bacteria carry out methyl transfer reactions, and thus could potentially methylate Hg, the only identified species to effect these reactions to date have been sulfate-reducing bacteria (Compeau and Bartha 1985; Gilmour et al. 1992). The basis for this apparent specificity has been investigated, but is still not well understood (Choi and Bartha 1993). On the other hand, field experiments in which sulfate-reduction has been inhibited by additions of molybdate have yielded appreciable levels of Hg methylation (Mack and Nelson, unpublished data) suggesting other bacterial groups may also contribute to methylation. Demethylation can occur by two or more pathways (Öremland et al. 1991); the importance of each pathway under different environmental conditions has not been well-characterized, but may result in different net rates of methylation.
Sulfate concentrations below 1 µM in freshwater systems inhibit the rate of methylation (Gilmour et al. 1992). The increases in Hg methylation observed in acidified temperate lakes can be attributed to sulfate fertilization rather than to direct pH effects. The high levels of sulfate in marine systems also inhibit methylation (Winfrey and Rudd 1990) by promoting precipitation of Hg as sulfides. The concentrations of sulfate in the waters of the Everglade (5-170 mg/L; Stober et al. 1995) span the 20-40 mg/L concentration range thought to be optimal for Hg methylation (Gilmour and Henry 1991). Thus, although sulfate concentrations in the Everglades have probably not changed appreciably (the high concentrations relative to other fresh waters are due to underlying mineralogy rather than acid rain inputs), the high levels of sulfates may predispose the system to respond strongly to removal of other limitations on methylation.

Other factors that may influence the rate of methylation include temperature, pH, DOC, and aeration status (Compeau and Bartha 1984; Miskimmin et al. 1992; Winfrey and Rudd 1990). Seasonal studies of microbial transformations of Hg indicate higher rates of methylation in summer than in winter (Bodaly et al. 1993; Korthals and Winfrey 1987). Given that most studies of microbial methylation have occurred in mid- to high-latitude lakes, the higher temperatures of the Everglades suggest potential rates of methylation in this system are unlikely to be limited by temperature as they are in temperate systems.

The aeration status of areas in South Florida may have changed in response to changes in hydrology and oxygen demand, as mediated by loadings of inorganic nutrients. Drainage of peat soils causes oxidation of organic matter from the soils, especially when microbial respiratory activity is enhanced by nutrient additions. The fate of any Hg associated with such soil loss in the Everglades is not known. Canalization and eutrophication may also have increased the extent of anaerobic zones within the water column, giving rise to areas of potentially high methylation activity. Additionally, eutrophication may increase activity of sediment microbial populations, making the sediments more strongly anaerobic. Such conditions favor activity of the sulfate-reducing bacteria responsible for methylation of Hg. Thus, eutrophication may affect the rate of methylation by both direct and indirect mechanisms.

Alteration of hydrology and nutrient status may also change the nature and composition of the organic matter cycled and transported within the system. In oligotrophic wetlands, much organic carbon is tied up as lignocellulose, or plant detrital material, which cycles slowly. Under more eutrophic conditions, algal growth and higher microbial activity increase the lability of the carbon. Increases in organic matter generally support higher microbial activity but may also complex the Hg, decreasing its availability for methylation. It is difficult, therefore, to predict the direction of change that may result from changes in character, amount, and distribution of organic matter.

**ABlOTIC BIOGEOCHEMICAL AND TRANSPORT PROCESSES**

**Background:** Mercury occurs in the environment as a number of species, which display species-dependent partitioning, bioavailability, rates of interconversion, and overall fate and transport. This section outlines ongoing and future research on those aspects of environmental inorganic Hg speciation that must be understood to assess Hg bioavailability in South Florida.

Of the various environmental species of Hg discussed in the scientific literature, monomethylmercury (CH$_3$Hg$^+$) is the dominant species associated with bioavailability and
biomagnification (Driscoll et al. 1994; Zillioux et al. 1993). Monomethylmercury typically represents ca. <1%-10% of the total Hg in a given water sample. Divalent Hg (Hg$^{2+}$) is the most thermodynamically stable species in oxic environments; it also may represent the dominant form of Hg in the water column and the dominant atmospheric species deposited either through dry or wet deposition. Elemental Hg (Hg$^E$) is presumably formed primarily through microbial reduction and, because of its high vapor pressure (Lindquist and Rohde 1985), may be the most significant volatile species lost to (and present in) the atmosphere. Dimethyl mercury ((CH$_3$)$_2$Hg) is another volatile species (Lindquist and Rohde 1985) that presumably can be formed in sediments, albeit at rates 6,000 times less than that of monomethylmercury (Wood 1974).

There is ample scientific evidence that many of the environmental Hg species are intimately associated with natural organic carbon (Alberts et al. 1974; Andren and Harriss 1973, 1975; Billen and Wollast 1973; Driscoll et al. 1994; Gill and Bruland 1990; Hurley et al. 1994; Lindberg and Harriss 1974; Robertson et al. 1987; Xu and Allard 1991; Zillioux et al. 1993). Unfortunately, a fundamental (mechanistic) understanding of Hg partitioning with natural organic carbon is not currently available. Without this understanding, a reliable analysis of the probable effect of restoration and management actions on Hg dynamics cannot be accomplished.

**Major Issues:** Although recreational use of the Everglades and other South Florida areas has been impaired by fish advisories, observed Hg concentrations in soils/sediments do not appear to be present at exceptionally high concentrations (Cantillo et al. 1993; Delfino et al. 1993; Long and Morgan 1990). Also, assuming monomethylmercury (CH$_3$Hg$^+$) is the dominant bioavailable species and South Florida is comparable to other environs, Hg methylation is likely to be most significant in surficial sediments (Billen and Wollast 1973; Callister and Winfrey 1986; Jernelov 1970).

The major issue is: What is the source of the Hg in the surficial sediments that becomes available for methylation? Is it Hg ultimately derived from external sources that is freshly deposited in the sediments? Or is it Hg migrating from deeper strata within the sediments? Answering these questions requires a technical capability for assessing Hg migration in sediments, which in turn requires the ability to assess porewater Hg concentration gradients established by background sedimentary biogeochemical processes. Technical projects designed to assist in answering the above questions focus on employing recent scientific advances in the understanding of sedimentary processes and speciation-dependent binding with organic carbon.

The two issues to be addressed in the near term are: 1) development of region-specific process models to describe Hg species-dependent binding with naturally occurring organic matter and 2) development of region-specific methods to assess Hg migration in sediments.