MERCURY IN THE 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.

Action to control or correct the problem of Hg contamination of the Everglades biota must await a better understanding of the sources and biogeochemical dynamics of the element. There are seven kinds of policy-relevant questions that must be answered (EPA 1993):

> What is the magnitude of the problem? What are the current levels of Hg contamination in various species? What ecological resources of interest are being adversely affected by Hg?
> What is the extent of the Hg problem? What is the geographic distribution of the problem? Is it habitat specific?
> Is the problem getting worse, getting better, or staying the same?
> What factors are associated with, or contribute to, MeHg accumulation in sensitive resources?
> What are the contributions and importance of Hg from different sources?
> What are the risks to different ecological systems and species from Hg contamination?
> What management alternatives are available to ameliorate or eliminate Hg contamination?

The EPA Region 4 Environmental Services Division is conducting field studies intended to delineate the extent, magnitude, and trends of the Hg problem and to generate data for the initial phase of a formal risk assessment (EPA 1993; Stober et al. 1992). All these activities are part of a larger interagency effort (SFWMD et al. 1994). The habitat types sampled include canals, ponds, sloughs, wet prairies, sawgrass marsh, and hammocks/tree islands. Canal sampling began in September 1993, with other tasks initiated in fall and winter of 1993-94. Water, soil, sediment, and biota are sampled using the EMAP probabilistic design. Regional air monitoring is being conducted by the Florida Atmospheric Mercury Study, supported by Florida Power & Light, Electric Power Research Institute, FDEP, and EPA. The Division is also participating in development of analytical capabilities for measuring Hg at the parts-per-trillion level in water and air.

This chapter describes the high-priority scientific investigations needed to develop the ability to predict the efficacy of policy alternatives. Sections are devoted to microbial methylation and demethylation dynamics, inorganic
chemistry, ecological dynamics, and aquatic and atmospheric modeling. Each section includes discussions of issues, current studies, and information needs. Figure 5 summarizes the information needs relative to restoration and science objectives.

**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 (Oremland 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.
Eliminate significant ecological and human health risks posed by mercury contamination.

**RESTORATION OBJECTIVES**
- Eliminate impact of external sources of Hg.
- Manage water and nutrients to sequester in-place Hg.
- Monitor ongoing damage and risk due to mercury contamination.

**SCIENCE OBJECTIVES**
- Inventory and characterize potential sources.
- Determine contributions of external and internal sources to present Hg contamination problems.
- Understand role of water and nutrients in Hg transport and mobilization.
- Understand impacts of Hg on health of Everglades biota.
- Measurements of reproductive and toxic impacts on biota.
- Delineation of food webs for impacted biota.
- Food web structure as function of restoration scenarios.
- Models of ecosystem response to Hg contamination.

**INFORMATION NEEDS**
- Emissions from urban sources.
- Hg speciation in emission streams.
- Hg vapor exchange rates.
- Vertical and horizontal transport fields.
- Spatial and temporal patterns of present deposition.
- Importance of species other than monomethyl-mercury.
- Present levels of contamination in water, soils, biota.
- Models of atmospheric chemistry, transport.
- Hg species binding to DOC: DOC/FPOM biogeochemistry.
- Porporewater chemistry and Hg migration.
- Rates of microbial methylation-demethylation and biogeochemical control forces.
- Models of Hg transport in canal-marsh landscape.

**Figure 6. Goal, objectives, and information needs for efforts on mercury.**
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.

**Major Issues**

An understanding of Hg transformation processes is critical to discerning and mitigating the sources of Hg in the system and reducing ecological exposures. Mercury species vary greatly in their physical properties, such as volatility, solubility, partitioning, as well as their bioavailability. Are the high levels of MeHg in fish and animals in the Everglades due to inputs of Hg or to internal transport and transformation? Examination of available data and consideration of hydrological and land-use changes that have occurred suggest that either or both phenomena may contribute to the current levels of contamination.

Existing Hg models represent microbial transformations of Hg as a single, first-order process resulting in the net production, or destruction, of MeHg (PTI 1994). Such models have been shown to be sensitive to the microbial transformation rate and to exchanges between benthic and water column compartments. Two major issues confound the useful representation of microbial processes in the models: 1) the inherent variability of experimental determinations of transformation rates (Gilmour and Henry 1991; PTI 1994) and 2) the lack of mechanistic understanding of the transformation processes. The latter is especially critical if models are to be used as insights into historical alterations of the Everglades system that may have contributed to mobilization and internal transport of Hg and as tools for predicting outcomes of mitigation scenarios.
Current Studies

Region 4 of the EPA is conducting a research program with the support of other Federal and State agencies. This program, R-EMAP, uses a probabilistic sampling strategy to determine distribution of MeHg and total Hg in water, sediments, and fish, as well as pertinent environmental parameters (e.g., temperature, DO, nutrient and sulfate concentrations, alkaline phosphatase activity, conventional soil parameters). Sampling efforts have been designed to support the testing of specific hypotheses for the distribution and transport of Hg; e.g., sampling efforts have followed longitudinal transects in canals and across nutrient (especially phosphorus) gradients. Present information indicates that the region of highest Hg concentration extends from WCA 3A south into the Shark Slough area of ENP. The zone within WCA 3 near the L-67 and Miami canals has the highest reported Hg concentrations for several species, including great white heron, mosquitofish, largemouth bass, and bowfin (COE 1995).

A preliminary laboratory investigation was supported by EPA to determine the effect of nutrient additions on methylation rates in microcosms (Kavanaugh and Barkay 1992). Methylation and demethylation were shown to be stimulated by additions of phosphorus to Everglades soils.

A field study jointly funded by the SFWMD, USGS, and FDEP was conducted between January 1992 and February 1993 to determine historical baseline concentrations of Hg in Everglades and Okefenokee sediments, post-industrial changes in sediment Hg accumulation, and spatial distribution of Hg throughout the Everglades (Delfino et al. 1993). This study found that average Hg concentrations in the surface sediments (n=51) was 121 ng/g and surface concentrations averaged 2.5 times higher than concentrations deeper in the profile. Extractable organic Hg averaged 52% (range 6-100%) of total; this fraction probably includes both MeHg and additional Hg species. Mercury accumulation rates started to increase ca. 1940, coincident with the mid-century alteration of hydrology and agricultural and urban development of South Florida.

A study plan has been developed to address concerns about Hg transformations and mobilization that might accompany the Everglades Nutrient Removal Project and the STAs proposed for cleansing agricultural runoff (SFWMD et al. 1994). Although the ENR is designed primarily to remove phosphorus, it also presents an excellent opportunity to test hypotheses regarding Hg transformations, especially those pertaining to effects of eutrophication and alteration of aeration status. In addition to manipulations planned for the ENR as a whole, microcosms and sediment material derived from the area will be suitable for testing responses to different concentrations of phosphorus or other experimental treatments. The ENR has been designed to mimic the hydrology of WCA 2A; no additional manipulations (physical, chemical or biological) are planned for enhanced removal of nutrients. It is projected that long-term nutrient removal will occur as a consequence of peat accumulation under anaerobic conditions; it is not known whether Hg will be sequestered or released under those conditions (Sugar Cane Growers Cooperative 1994).

As part of EPA and FDEP permitting requirements, total recoverable Hg and MeHg will be monitored at the inflow and outflow of the ENR site, as well as at a location upstream of the outflow in the L-7 Borrow Canal. Requirements of the permit also stipulate that body burdens in fish and shellfish be monitored for 2 years of operation. Fluxes of total, particulate, and dissolved Hg will be measured to determine the mass balance of Hg species, as will rates of Hg accumulation in sediments. An atmospheric Hg monitoring station, operated by the Florida Atmospheric Monitoring Study, has been constructed to measure atmospheric fluxes to the site.

The SFWMD (1993) has also proposed studies under the Section 319 Non-point Sources Grants Program to determine the effects of Best Management Practices implemented in the EAA on Hg loadings to the Everglades. Three categories of practices will be evaluated: 1) traditional on-farm changes in water and fertilizer application practices, 2) buffer strips or retention ponds, and 3) a large-scale constructed wetland to be managed by a consortium of farmers.

The USGS has been investigating the interactions between hydrological and chemical processes and distribution of MeHg, focusing on the speciation and complexation of Hg. It also is investigating the controls on methylation processes by manipulating sediment cores from canal and marsh locations within the Everglades. This effort is being coordinated with other Federally funded projects and includes co-location of sampling with R-EMAP sites.
In addition to the R-EMAP sampling effort supported by EPA Region 4, EPA plans to support basic investigation into the mechanisms that control net rate of Hg methylation with the goal of developing models for the kinetics of the process. Two projects have been funded. One will investigate the response of demethylation processes to environmental factors and the resultant effect on net methylation rates, along with the role of methylating agents. The second will investigate the environmental processes that control the rate of methylation. Efforts will be made to determine methylation/demethylation rates in materials derived from R-EMAP sampling sites. Results of these experimental investigations will be incorporated into development of biogeochemical models that link microbial transformations of Hg with carbon, sulfur, and nutrient cycling.

The proposed integrated program also includes creation of a GIS database for environmental parameters that may control transport and transformation of Hg in South Florida (e.g., soil types; vegetation; hydrology; agricultural crops; wildlife distribution; fertilizer and pesticide applications; nutrient concentrations; water chemistry; and Hg concentrations in soils, sediments, and water).

**Information Needs**

**Critical Questions**

Given the role of MeHg in uptake and accumulation of Hg by biota, an understanding of the formation and fate of this compound is essential for development of risk assessments and ameliorative strategies. Such an understanding must be based on a science program that addresses the following questions:

> What are the environmental factors that influence rates of microbial methylation and demethylation? How are these factors constrained by present conditions and historical changes in hydrology and land use of the Everglades? Changes in nutrients, oxygen, and organic carbon must be considered.

> How do organic matter and alterations of organic matter that may result from changing nutrient and oxygen status affect availability of Hg for microbial transformations and the activity and composition of microbial populations that carry out the Hg transformations?

> How do ecological zones and/or land uses influence rates of methylation and demethylation? Can characterization of such zones be used to construct a mass balance and transport model for Hg in the Everglades?

> What is the impact of alterations of aeration status, such as that resulting from periodic inundation and dewatering of agricultural lands, on release and transformation of Hg?

> Do forms of organomercury other than MeHg occur in waters and sediments of the Everglades? If so, what are the implications of other organomercury forms for transformation pathways and bioaccumulation?

> Do demethylation processes differ under different aeration regimes and in different ecological zones? What is the impact of oxidative versus reductive demethylation pathways on the net rate of methylation?

A science program that addresses these questions will support construction of a biogeochemical model that integrates methylation of Hg with carbon, nitrogen, phosphorus, and sulfur cycles. Such a model will link microbial activity with environmental parameters to test explanatory hypotheses for fate and transport of Hg and predict the consequences of mitigation strategies.

**Approach**

Two complementary approaches are essential to resolve questions on the sources and fate of Hg within the Everglades: 1) determination of distributions, and 2) experimental investigations of transport and transformation processes. Both efforts are critical for distinguishing among the hypotheses proposed to explain the high concentrations of MeHg in biota. Recent and ongoing research focuses on determining the extent of Hg contamination; current distribution of Hg species in sediment, water and fish; and historical distribution of total Hg in sediments.
Models for the rates of Hg transformations, as derived from the process-based investigations, must be tested and implemented based on specific geographic data. Initially, a mass-balance approach could be used to estimate Hg transformations associated with large-scale land use and ecological zones. Subsequent efforts would implement Hg transformation models within the Hg cycling and transport models.

Also needed is appropriate characterization of ecological zones and land uses, both present-day and historical, in the Everglades with respect to conditions that influence rates of M/D, in order to integrate and analyze data on the forms and concentrations of Hg.

Specific needs not directly addressed in current or proposed research plans include:

> Origin of the organic matter (e.g., periphyton vs. detritus of emergent plants) that serves as the microbial substrate for methylation, as it is impacted by altered nutrient and aeration conditions.

> Effects of periodic inundation of agricultural lands.

> Importance of organomercury species other than MeHg.

ABITIC 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$^0$) 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; Delphin 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.

Current Studies

Current investigations on the abiotic processes relevant to Hg speciation are being conducted primarily via an Interagency Agreement between the EPA and USGS. These efforts include developing an experimental dataset of Hg binding with natural organic carbon (obtained from the South Florida Region), developing fundamental process-based models of observed Hg species-dependent binding behavior, and investigating the potential migratory behavior of Hg in sediments from the South Florida Ecosystem. This last aspect builds (in part) on application of a steady-state sediment model produced under an existing cooperative agreement between EPA's Environmental Research Laboratory-Athens and the Georgia Institute of Technology (A General Transport Reaction Model for Freshwater Sediments; Van Cappellen and Wang, in press).

Information Needs

Critical questions

Divalent and monomethylmercury are known to exhibit substantial binding with natural organic carbon under most oxic environmental conditions. Although this binding is significant to environmental fate, methylation, and ultimate bioavailability, the mechanistic processes involved are not well understood. Are the binding properties of natural organic carbon in South Florida commensurate with the properties of organic carbon found elsewhere? Does ionic Hg in South Florida bind with natural organic carbon in a manner comparable to binding observed elsewhere? What quantitative predictive relationships can be developed to assess Hg binding with natural organic carbon?

Elevated total Hg concentrations have been observed in surface sediments in South Florida (Delfino et al. 1993). Are these elevated sedimentary Hg contents the primary source of monomethylmercury to the biosphere or do these elevated surface concentrations merely co-vary with elevated external loadings? Is there a depth in the sedimentary column where Hg becomes relatively non-bioavailable? Will Hg in these sediments experience ecologically significant post-depositional migration?

Approach

Findings obtained from the current research will be applicable as general, process-based methods for assessing environmental Hg speciation and potential sedimentary migration. Because these findings will be the products of more basic investigation, future applications will involve extrapolating relationships derived from carefully controlled laboratory systems to ecological environments (within a framework of statistical uncertainty).

ECOLOGICAL EXPOSURE AND EFFECTS

Background

Mercury contamination in aquatic communities of South Florida is a well documented problem and may be an important contributing factor to the decline of wading bird populations and other top predators, such as the Florida
The ability to accurately predict Hg bioaccumulation is needed to define realistic dietary exposures to wildlife, assess the potential for significant biotic transport of Hg, and predict the onset of residue-based effects that would be realized fully, decision makers must be able to predict and assess the ecological risk posed by Hg in conjunction with other restoration objectives.

Two basic approaches have been used to quantify the bioaccumulation of environmental pollutants in aquatic and terrestrial biota. The first of these assumes that organisms quickly achieve a chemical equilibrium with respect to a particular media or route of exposure. For aquatic biota, this reference media is generally considered to be the water. For terrestrial plants, on the other hand, the reference media may be the soil or possibly air. For terrestrial animals, the reference media may be either the soil or, more commonly, the animal's principal food items. This approach uses bioconcentration or bioaccumulation factors (BCFs or BAFs) to estimate chemical residues in biota from measured concentrations in the appropriate reference media. BCFs for a variety of mercuric compounds in diverse biota have been reported to vary between $10^{2.4}$ and $10^{6.7}$. Because bioaccumulation/elimination half-lives of most mercuric compounds are extremely long, however, many of the BCFs reported to be less than $10^4$ do not represent true equilibrium values. For example, half-lives of MeHg in most vertebrates vary from months to years. Moreover, these half-lives generally will depend on body size and environmental variables such as temperature. The second approach to predict chemical bioaccumulation assumes that chemical exchange is a slow process and that the organism's body burden is not necessarily in equilibrium with any particular exposure media. This approach, which appears to be more appropriate for Hg, predicts bioaccumulation using mathematical models that explicitly simulate the chemical's uptake, metabolism, excretion, and biodilution as a function of the organism's environmental exposures.

Many scientists have studied the bioaccumulation of Hg in diverse biota under natural field conditions. In many cases, these studies have demonstrated a strong correlation between the organism's body size and its body burden of Hg. This trend, which is particularly evident in fish, mollusks, and aquatic mammals is influenced by several factors. Increasing body size, for example, is generally associated with increasing longevity and hence increased temporal exposure; this is a consideration that is extremely important for slowly accumulating chemicals. Increasing body size also increases an animal's exposure to Hg along spatial dimensions. Territory size and home ranges of many vertebrates, for example, are positively correlated with their body size. Given two animals with different sizes of foraging ranges, it is natural to expect the animal with the larger range would be much more likely to encounter contaminated prey than the other. Allometric relationships between body size and feeding also influence this general trend. The simple fact that large animals consume more prey than do small animals obviously increases their exposure probabilities, as does size-dependent home ranges or territories. Another factor contributing to this bioaccumulation trend is that as many predators grow they generally tend to consume larger prey. This trend is particularly evident in predatory fish but is also demonstrated by other predators including snakes and birds. If the Hg concentration in a predator's prey displays a positive correlation with the prey's body size, predators that exhibit size-dependent foraging will be subject to ever-increasing Hg exposures.

These kinetic and allometric considerations strongly suggest that realistic analysis and characterization of Hg contamination in South Florida must be performed using dynamic, process-based bioaccumulation models. This conclusion is also supported by the fact that several authors have shown that total body burdens of Hg in fish and other aquatic biota are often correlated with environmental variables not accounted for by BCF/BAF approaches. For example, Hg burdens are often negatively correlated with water pH and DOC. Whereas the negative correlation between body burden and ambient pH is generally attributed to reduced methylation of Hg under alkaline conditions, the negative correlation between body burden and ambient DOC is generally believed to result from reduced bioavailability of Hg as it binds to sulfhydryl groups of organic molecules. Significant positive and negative correlations between total body burden of Hg in fish and lake size also have been reported. Positive correlations may be explained by the simple fact that large lakes are generally situated in larger watersheds than are small lakes. If atmospheric deposition is the area's most significant Hg source, large lakes would be expected to have higher Hg concentrations than small lakes. The same logic would also hold for large vs. small water impoundments overlying potential sedimentary sources of Hg. Negative correlations, on the other hand, may be explained by the trend of small lakes to have higher average temperatures than large lakes and the positive correlation between rates of MeHg production and temperature (Bodaly et al. 1993).
result from chronic or varying temporal/spatial exposures. Most models of MeHg are very sensitive to changes in elimination rate (Norstrom et al. 1976; Rodgers 1994). There are, however, few rigorous studies of MeHg elimination in fish and no detailed studies of MeHg elimination in fish since the 1980s. The Norstrom equation describing MeHg elimination assumes it is independent of metabolic rate, but MeHg elimination in rainbow trout was significantly affected by meal size and presumably metabolic rate (Rodgers and Beamish 1982). If metabolic rate significantly affects MeHg elimination in fish, the effects would be most pronounced in small prey fish at South Florida temperatures. Similarly, the value used for assimilation of dietary MeHg (reported values range from <20% - >80%) will significantly affect MeHg bioaccumulation (Norstrom et al. 1976; Rodgers 1994). Accordingly, detailed laboratory and field studies of uptake and elimination of MeHg in representative South Florida species of predatory and prey fish and selected invertebrates under Florida environmental conditions should be undertaken. Results of these studies would then be incorporated into models of MeHg bioaccumulation.

Major Issues

Most ecotoxicological studies of Hg have focused on determination of traditional exposure-based endpoints such as LC₅₀s. These data can differ by two or three orders of magnitude depending on the organisms or life stages considered. Such variations, however, are not surprising since any factor that influences rate of Hg accumulation within an organism should be expected to affect its observed LC₅₀s. Thus, for example, factors that affect respiration of aquatic biota, and hence their gill exchange, should also affect the LC₅₀s of those organisms. Thus, it is not surprising that the LC₅₀s for most aquatic biota are generally decreasing functions of body size, temperature, and duration of exposure. For marine biota, LC₅₀s also depend on salinity.

Although most ecological risk assessments for environmental contaminants traditionally have been founded on exposure-based endpoints such as LC₅₀s and EC₅₀s, effects of chemicals on organisms are not caused by the chemical in the environment but rather by the chemical that is accumulated within the organism. Exposure-based toxicity endpoints have many inherent limitations. Generally these endpoints address only a single route of exposure under constant exposure conditions. For example, acute hazard assessments for fish usually are based on 96-hr LC₅₀s for constant water concentrations. Under field conditions, however, fish will accumulate chemicals not only from the water but also from their prey that also become contaminated. If dietary exposures are more significant than direct aqueous exposures, there is no apriori reason to assume hazard assessments based on LC₅₀s would be protective of field populations. Even if both dietary and aqueous toxicity benchmarks are known, there are no rules-of-thumb to determine which toxicity benchmark should be used for all fish or all field exposure scenarios, since the relative significance of various routes of uptake depends on the exposure scenario being considered.

The only objective way to address the consequences of Hg exposure to South Florida biota -- and hence to reduce uncertainties associated with ecological risk assessments of Hg -- is to deal directly with the kinetics of chemical bioaccumulation in organisms and establish appropriate residue-based endpoints.

Current Studies

Several conceptual models describing food webs and habitat utilization in the South Florida Ecosystem have already been developed (see Davis and Ogden 1994). These models document the principal ecological interactions and forcing functions needed to sustain viable populations of the major wildlife species. While most vertebrate wildlife are treated as individual species, invertebrate wildlife are typically treated as functional groups. Several studies have focused on exposure of individual species or ecological guilds to Hg. Wood et al. (1993) used blood and feather samples and carcasses to assess Hg exposures in bald eagles; Sundlof et al. (1994) summarized data for exposure in wading birds. Jurczyk (1993) constructed a preliminary ecological risk assessment for species including the Florida panther and American alligator. Summaries of ecological exposures to South Florida biota are available as abstracts presented at the international meeting, "Mercury as a Global Pollutant (1994)."

The NBS and NPS are currently developing, via the ATLSS program, physiologically based models for several key species of Everglades wildlife, including the American alligator, wood stork, white ibis, snail kite, Cape Sable seaside sparrow, Florida panther, and white-tailed deer. ATLSS considers the impacts of habitat and contaminant stresses (including Hg and other compounds) as mediated by trophic transfers. EPA's Ecosystems
Research Division in Athens, Georgia, has begun modification of the FGETS (Food and Gill Exchange of Toxic Substances) bioaccumulation model to analyze bioaccumulation of Hg in Everglades fish communities. FGETS is a process-based model that describes the bioenergetics and bioaccumulation of organic chemicals of arbitrarily specified age-structured fish assemblages.

Habitat suitability models for vertebrate wildlife species will be reviewed and used as an integral part of this research. These models should be used as the initial, but not necessarily final, frameworks to address the foraging, nesting/reproductive, and roosting habitat requirements of vertebrate wildlife species of concern. A realistic forest stand model (e.g., FORET, FOREST, JABOWA, KIAMBRAM, SILVA, SWAMP) will be integrated with a wetland foodweb model in order to simulate the structural characteristics of wetland vegetation required by wetland vertebrates for food, shelter, and reproduction. This stand model should be responsive to hydrologic alterations, fire, local and regional climatic factors, and episodic disturbances such as hurricanes.

Information Needs

Critical questions

Over the last 20 years, considerable attention has been focused on monitoring and investigating the bioaccumulation and ecological effects of Hg. Although several review papers have been published on various aspects of ecological exposure and effects of Hg (Depledge and Rainbow 1990; Driscoll et al. 1994; Eisler 1987; Gavis and Ferguson 1972; Jonnalagadda and Prasada Rao 1993; Richman et al. 1988; Sorensen 1991; Zalups and Lash 1994; Zillioux et al. 1993), many aspects of these topics remain unknown or unsynthesized. Major questions regarding Hg bioaccumulation include:

- What is the partitioning and binding behavior of different Hg species within organisms?
- Is the heterogeneous distribution of Hg among tissues a kinetic or equilibrium phenomenon?
- How should Hg bioconcentration in plants be modeled to describe trophic exposures to herbivorous wildlife?
- How do prey availability, size-dependent home ranges, and ontogenetic changes in prey preferences influence bioaccumulation of Hg in aquatic and terrestrial wildlife?
- How does the spatial and temporal distribution of habitat influence bioaccumulation of Hg in highly mobile and migratory wildlife?
- What metabolic transformations of Hg occur that affect its uptake, internal distribution, or excretion?
- Can Hg bioaccumulation be modeled with sufficient accuracy without modeling the concurrent bioaccumulation of other metals that compete for the same sulfhydryl binding sites?
- What water quality parameters (including temperature) influence bioaccumulation of Hg in Everglades aquatic communities? What fate and transport models can be used to simulate these variables?

Major questions regarding ecological effects of Hg include:

- What bioconcentration or bioaccumulation models are available to estimate residue-based toxicity endpoints from previously published exposure-based endpoints?
- What residue levels affect feeding, growth, reproduction, and mortality of South Florida wildlife? What indicator species should be selected for study?
> How should the accumulative effects of multiple mercuric species be quantified? How should the accumulative effects of Hg, other metals, and organics be quantified?

> What factors ameliorate Hg toxicity (e.g., selenium species)? How should these factors be incorporated into the Hg modeling program?

**Approach**

To estimate accurately the ecological effects of Hg in the South Florida Ecosystem, a suite of process-based models supported by user interfaces and databases must be developed to describe the:

> nominal trophic dynamics and habitat utilization of vertebrate and invertebrate wildlife in wetland and estuarine ecosystems,

> effects of hydrology, water quality, and vegetative habitat structure alterations on these ecological processes,

> bioaccumulation of Hg and other persistent organic chemicals and metals in wetland and estuarine biota, including interactions between contaminants, and

> direct and indirect effects of chemical contamination on structure and function of wetland and estuarine ecosystems.

Conceptual models describing food webs and habitat utilization in the South Florida Ecosystem should be documented to delineate the principal ecological interactions and forcing functions needed to sustain viable populations of the major wildlife species. While most vertebrate wildlife should be treated as individual species, invertebrate wildlife could be treated as functional groups. Aquatic and terrestrial flora should be characterized at a scale of resolution appropriate to describing the trophic and habitat dependencies of these wildlife components.

Physiologically based models being developed for South Florida wildlife (see above) already address some of the above needs and should be continue to be supported. EPA/ERD-Athens will be modifying the FGETS bioaccumulation model to analyze bioaccumulation and effects of Hg in the South Florida Ecosystem. Because of its generalized structure, other wildlife components can be readily incorporated into the existing FGETS foodweb structure.

Habitat suitability models for vertebrate wildlife species will be reviewed and used as an integral part of this research. These models should be used as the initial, but not necessarily final, frameworks to address the foraging, nesting/reproductive, and roosting habitat requirements of vertebrate wildlife species of concern. A realistic forest stand model (e.g., FORET, FOREST, JABOWA, KIAMBRAM, SILVA, SWAMP) will be integrated with a wetland foodweb model in order to simulate the structural characteristics of wetland vegetation required by wetland vertebrates for food, shelter, and reproduction. This stand model should be responsive to hydrologic alterations, fire, local and regional climatic factors, and episodic disturbances such as hurricanes.

Wetland and estuarine community models should be validated piece-wise using literature data and field and laboratory studies planned as part of the South Florida Ecosystem Restoration. As various submodels are validated, databases of ecological, morphological, and physiological parameters required by the submodels will be compiled to facilitate rapid and effective model parameterization. User interfaces also will be developed.

**AQUATIC MERCURY FATE MODELING**

**Background**

Conceptual models and process submodels of the biogeochemical cycling of Hg, properly distilled, provide a powerful basis for operational site-specific models. Such Hg fate models may be constructed de novo or may be built upon the framework of existing chemical transport and fate models. Several existing chemical models treat
environmental transport and chemical transformation processes in a general manner that can be used for many organic and inorganic chemicals. These models can be modified to handle the special transfer and transformation reactions that affect mobility and speciation of Hg. This section discusses development and application of a Hg fate model to specific locations in the Everglades.

Several modeling approaches for describing fate of Hg in watersheds have been undertaken. Recent modeling efforts have usually been based on several simplifications. Some are simplistic in their representation of Hg chemistry. Others, although able to represent some of the complex Hg chemistry, can represent only simple physical environments. Currently, a general modeling framework for the mechanistic simulation of transport and fate of Hg in complex aquatic environments does not exist.

The Mercury Cycling Model mechanistically simulates transport and transformations of Hg in natural lakes (Hudson et al. 1990, 1994). Four Hg components are simulated: Hg(0), Hg(II), MeHg, and Hg(inert). Kinetic transformation reactions are linear with respect to the Hg components but may be modified by other water quality variables. The model handles aqueous complexation using compartment-specific parameters and equilibrium constants. A simple food-chain model is included with direct transfers of Hg through a linear four-step food chain composed of phytoplankton, zooplankton, planktivorous fish, and piscivorous fish. MCM is spatially simple, calculating Hg fate and bioaccumulation in three compartments (epilimnion, hypolimnion, benthic sediment).

MERC4 (Martin 1992) is based on a generalized compartmental modeling system that allows complex physical representation of water bodies with up to 500 segments that can be linked with hydrodynamic models (Ambrose et al. 1987). MERC4 Hg components and reactions were set to emulate MCM; Hg(0), Hg(II), MeHg, and Hg(inert) are simulated with aqueous complexation, solubility, sorption, and kinetic transformation reactions. In addition, MERC4 conducts mass balance calculations for three user-defined solids. The current version of MERC4 does not include food chain components. It is presently undergoing limited inhouse and external testing, but has not been formally reviewed or released. A beta-test version of MERC4 was modified by PTI, Inc., to include simple bioaccumulation routines and successfully applied to Onondaga Lake, an urban lake in the Northeast. Fish Bioenergetics Model 2, developed at the University of Wisconsin Center for Limnology, was used to estimate Hg accumulation in the aquatic food chain based upon prey consumption, waste production, mortality, and fish growth. The food chain is composed of phytoplankton, zooplankton, macroinvertebrates, and seven fish species, including planktivores, demersals, and piscivores.

RMA-4 is a simple two-dimensional, depth-averaged finite-element water quality model that handles contaminant transport and first-order decay (King and Rachiele 1989). This model is linked with a compatible hydrodynamics program and software for mesh generation and post-processing. The University of California-Davis is modifying the RMA-4 model to simulate sediment and Hg components, including Hg(0), MeHg, and Hg(II). Both MeHg and Hg(II) are allowed to distribute between dissolved and particle-bound forms. Biological and chemical transformations of Hg from one component to another are modeled as either zero- or first-order sources or sinks. Among the transfer and transformation processes modeled are methylation, demethylation, volatilization, sorption-desorption, sedimentation, reduction, bio-uptake, atmospheric deposition, and diffusion.

Major Issues

Mercury fate is multimedia in scope. Because of the size and complexity of any general multimedia Hg model, efforts have generally been directed to individual media, although it is recognized that Hg can exchange between the atmosphere and surface water. Although aquatic food-web bioaccumulation models are often formulated separately from surface-water models, the nature of Hg dynamics requires a direct connection between the models. The major issues in constructing a Hg model are: 1) devising a proper and practical representation of the complex physical, chemical, and biological reactions, and 2) integration of the major components into an operational framework. The major issues in operating a Hg model are: 1) proper parameterization, given measurement and model uncertainty, and 2) spatial and temporal variability.

Current Studies

Both UC-Davis and ERD-Athens plan to pursue modeling investigations of Hg transport, fate, and bioaccumulation in Clear Lake. In a current contract, UC-Davis is developing a general Hg food-web model and parameterizing it for Clear Lake. UC-Davis plans to incorporate this model into a general biogeochemical modeling
system that simulates aqueous and benthic inorganic and MeHg concentrations throughout Clear Lake and exercise the modeling system to investigate consequences of potential remediation options. The resulting model will describe a simple aquatic food web that incorporates transfers to piscivorous birds and mammals. This model will be parameterized and validated with data from Clear Lake but will be designed so it can be applied to other aquatic systems by respecifying parameter values.

ERD-Athens is funding a National Research Council associate to investigate model linkage issues, particularly interactive coupling of hydrodynamic, water quality, and bioaccumulation models through parallel processing. Clear Lake will be the test system for this work. In addition, ERD-Athens has made plans to study Hg transport and fate within canal and marsh systems in the Everglades, in cooperation with EPA Region 4 R-EMAP studies. Some modeling components used in this study will be derived from the modeling package arising from the Clear Lake study. Two modeling tasks have been identified.

The goal of the first task is to predict the fate of Hg species in the sediments, water, and fish of both a selected canal system and a marsh system in the Everglades, based upon known sources. The first step in this task is to calibrate flow, sediment transport, and Hg transport in the selected aquatic systems. Based on results of the initial application and ongoing studies, the Hg transport model will be revised and extended. Food-web bioaccumulation will be simulated using the food-web model originally developed for Clear Lake.

The goal of the second modeling task is to predict the fate of Hg species in the sediments, water, and fishes of the Everglades, based upon known sources. The first step is to identify and code a simplified Hg dynamics model for linked canal-wetland-sediment compartments. This simplified model will be applied first in a simple compartment modeling framework for screening investigations, then later to the Everglades system as a whole, with proper hydrologic and atmospheric linkages specified from existing models. Issues of scale and model linkage will be investigated in both tasks.

Once the models for the canal, marsh, and Everglades system have been constructed, calibrated, and tested, sensitivity analyses will be conducted to explore the relative contributions of various sources and processes. Among potential sources to be analyzed are atmospheric deposition and exchange, oxidation of peat, methylation and exchange of historic benthic deposits, and runoff of nutrients and organic material from agricultural areas. Loading, transport, and benthic exchange under both average conditions and large-storm conditions will be studied.

Ongoing and planned hydrologic research and model development described in the chapter on modeling (in this document) should provide important input to application of these Hg models.

Information Needs

Critical questions

Level of process aggregation. Existing chemical fate models such as the TOXI5 component of WASP5 can simulate generic transformation processes among three chemicals as defined by the user. This model can be set up to describe partitioning, volatilization, oxidation, reduction, methylation, and demethylation reactions for dissolved, DOC-complexed, and sorbed phases of Hg(0), Hg(II), and MeHg. Models such as MCM and MERC4 add specific equilibrium complexation reactions to these kinetic reactions and allow more detailed chemical process description. A general modeling issue is matching the complexity of process description to the available scientific knowledge, available site-specific data, and level of analysis required.

> What value is gained in screening-level calculations and in management scenario analysis by increased levels of process description?

Level of spatial aggregation. The models outlined here have generally been parameterized for individual ponds, streams, and lakes. The computational networks generally have a longitudinal spatial resolution of 0.5-5 km (0.3-3 mi); the vertical resolution is typically 1-10 m (3.3-33 ft) in the water column and 1-100 cm (0.4-39 in) in the benthic sediment.
> What level of spatial aggregation in the benthic sediments is necessary to accurately capture the important biochemical transformation processes?

> How can a large network composed of canal and marsh elements be constructed to efficiently and accurately represent transport of Hg through large regions, such as a WCA or the Everglades as a whole?

**Level of model linkage.** The models described here represent chemical transport and fate processes in aquatic systems. Some have been linked to atmospheric and terrestrial models through external loading files. This is the most efficient approach when inter-media transport is predominantly feed-forward. Major questions to be answered in constructing a South Florida Hg modeling system include:

> What is the degree of feedback between aquatic, atmospheric, and terrestrial environments?

> How can these inter-media transfers can be efficiently and accurately represented?

**Approach**

Some of the existing Hg models are simplistic in their representation of Hg chemistry, while others represent only simple physical environments but incorporate a more realistic representation of Hg chemistry. MCM has become a standard for handling Hg components and reactions. Operational models are needed that can represent a complex physical environment and handle complex Hg chemistry in a manner similar to MCM. These are still under development and testing and require linkage with a food-web component.

Reliable diagnostic or predictive modeling depends to a great extent on accurate process descriptions. The most important areas of process uncertainty expected to affect overall Hg fate are highlighted below. The proper application of these models requires the specification of input data that describe and parameterize the environment being investigated. Data needs are also discussed below.

**Site-specific data needs.** For aquatic fate models, data needs include hydrogeometry, advective flows, dispersive transport, external loadings and boundary concentrations, and various chemical constants and environmental parameters. The chemical constants and environmental parameters required for Hg modeling will depend upon how the speciation and transformation processes in the model are formulated. Some environmental parameters expected to be important include pH, DO, DOC, sulfide, sulfate, and total dissolved solids.

**Methylation and demethylation kinetics.** The methyl forms of Hg are known to bioaccumulate strongly and provide the most risk to humans and wildlife. Most of the Hg delivered to the aquatic environment is inorganic. The internal production of MeHg, then, is a crucial process in any mechanistic Hg fate model. The form of the kinetic equations, dependencies on environmental parameters, and rate constants must be described and tested in a variety of aquatic environments.

**Complexation with fine organics, DOC, and colloids.** Those species of Hg that are complexed with dissolved or fine organic material are mobilized for transport but may be shielded from some loss processes. Good process models should be able to describe the binding capacity and strength of this material for various species of Hg. In addition, the biogeochemistry of DOC and fine organics in canals and wetlands must be described. Formation and loss processes must be quantified.

**Sorption onto sediments.** Those species of Hg that sorb onto suspended sediments can be deposited into the benthic environment and transformed or buried. Process models are needed that can accurately describe the sorption process for the important species of Hg. In addition, data are needed to characterize the sediments in South Florida so that their sorption capacity can be modeled. Sediment transport processes through canals and wetlands must be described, especially for silt and clay fractions. Deposition and scour processes must be described under both average conditions and during large-storm conditions.

**Uptake by aquatic plants, phytoplankton.** The amount of partitioning or uptake of Hg into the base of the aquatic food web drives subsequent bioaccumulation. Investigation is needed into how this can best be represented,
the coefficients or rates for Hg species entering phytoplankton and plants, and what environmental parameters might affect the kinetics.

**Spatially distributed food-web model.** The current generation of food-web models describes bioaccumulation in one place. For large or long aquatic systems with gradients of exposure concentrations, a spatially distributed food-web model will be necessary. Such a model would allow the user to specify a range for each fish species and age class. Plankton would be carried through the spatial network by advective currents. Overlapping ranges would be taken care of properly. Part of this effort requires the accurate biological description of the site being investigated. Modeling technology must be developed to facilitate representation of the biology and perform the bookkeeping properly.

**Parallel linkage of aquatic fate and food-web models.** Traditional aquatic chemical fate models do not include an internal food web. In these models, bioaccumulation calculations are executed following the aquatic fate calculations, as the aquatic concentrations are not usually affected significantly by the food web. Aquatic fate and bioaccumulation cannot be treated separately for MeHg, however, because a significant portion of the MeHg in the water column can be found in fish. Models such as MCM and Meridian have food-web equations built in, and the Wisconsin bioenergetics model has been used as a subroutine to MERC4. A general modeling linkage should be developed to allow the operation of specialized food-web models with spatially distributed aquatic fate models, including feedback between the two.

### ATMOSPHERIC MERCURY FATE MODELING

**Background**

Atmospheric models of Hg transport and transformation are being constructed and used to determine human exposure to Hg from various anthropogenic sources. This section reviews operational atmospheric Hg fate models that could be adapted for use in South Florida. Present atmospheric Hg fate models are built upon the framework of existing chemical transport and fate models. These models can be modified to handle the special transfer and transformation reactions of Hg and its compounds. This chapter focusses on one long-range model that is being used to examine Hg transport, along with some of the process and data uncertainties encountered.

Following a decade of development in Europe and the U.S., the REgional Lagrangian Model of Air Pollution (RELMAP) was produced in 1984 (Eder et al. 1986; Clark et al. 1992). RELMAP is capable of simulating concentrations and wet and dry deposition patterns of SO$_2$, SO$_4^{2-}$, and fine and coarse particulate matter. In addition to the main model program, the complete RELMAP modeling system includes 19 preprocessing programs that prepare gridded meteorological and emissions data for use in the main program. Currently, the RELMAP is supported by EPA's Atmospheric Research and Exposure Assessment Laboratory.

The original sulfur version of RELMAP was recently modified to permit simulation of atmospheric Hg. The goal was to model the emission, transport, and fate of airborne Hg over the continental U.S. for the year 1989. Modifications to RELMAP for atmospheric Hg simulation were largely based on recent Lagrangian model developments in Europe (Petersen et al. 1994). The Hg version of RELMAP was developed to handle three species of Hg -- elemental (Hg$^0$), divalent (the mercuric ion, Hg$^{2+}$), and particulate Hg (Hg$_{part}$) -- and carbon soot. Recent experimental work indicates both ozone (Munthe 1992) and carbon soot (Brosset and Lord 1991; Iverfeldt 1991; Lindqvist et al. 1991) are important in determining the wet deposition of Hg$^0$. Carbon soot, or total carbon aerosol, was included as a modeled pollutant in the Hg version of RELMAP to provide necessary information for the Hg$^0$ wet deposition parameterization. Observed O$_3$ air concentration data are used directly and not explicitly modeled. Methyl mercury was not included in the Hg version of RELMAP because it is not yet known if it has a primary natural or anthropogenic source, or if it is produced in the atmosphere.

**Major Issues**

Atmospheric models are generally used to estimate direct human exposure and provide loadings to surface water and soil. Volatile exchanges, however, could provide significant loadings from watersheds to the air. Although
terrestrial and aquatic fate models are often formulated separately from atmospheric models, the nature of Hg dynamics requires an interconnection between these models that is achieved only crudely at present. There are significant uncertainties about atmospheric Hg chemistry that could affect the accuracy of descriptions of deposition of Hg species at the local and regional scales.

**Current Studies**

**Development of Eulerian model**

The Atmospheric Characterization and Modeling Division of EPA/AREAL has proposed the development of a long-range atmospheric transport and transformation model using the Eulerian reference frame of the Regional Acid Deposition Model (RADM). This model will include internal nesting so subregions can be examined in detail within a framework that provides boundary concentrations from long-range transport. Given adequate support, 2 years would suffice to make this model operational.

**Application of Eulerian model to South Florida**

The Eulerian atmospheric transport model will be modified for Hg constituents and applied to the South Florida region. Vapor concentration and deposition data will be provided at a set of atmospheric monitoring stations covering eastern, central, and western South Florida. An inventory of Hg sources will provide the loadings to the model. A series of calibration simulations will cover the period of data collection and will focus on uncertain processes and model parameters. Following calibration, another series of simulations will be conducted to predict long-term atmospheric Hg trends given various management options.

**Information Needs**

**Critical questions**

**Vertical Model Domain.** The RELMAP model top is defined to be the maximum vertical extent of the convectively driven mixed layer. Monthly values defined from mixed-layer-height climatology are rough estimates of a meteorological phenomenon that may not exist in many situations. Although a surface-based mixed layer may be well defined, pollutants that persist in the atmosphere for long periods of time are certain to mix to some degree into the free atmosphere above the mixed-layer top. Elemental Hg deposits relatively slowly through precipitation processes due to its low water solubility, and its dry deposition appears to be minimal since it is in vapor form under normal atmospheric conditions. Elemental Hg does appear to be quite persistent in the atmosphere.

Because RELMAP does not simulate the flux of air or pollutants through the height of the mixed layer, which is fixed for each monthly simulation, the use of horizontally divergent/convergent wind fields to define the motion of the pollutant puffs can sometimes result in unrealistic instantaneous concentration fields. RELMAP was not designed to provide instantaneous realizations of pollutant concentration fields. Rather, it was designed for seasonal and annual simulations where the total effects of convergent and divergent wind fields can balance one another. There is, however, some uncertainty as to whether this balance actually occurs in all situations.

**Aqueous Chemistry.** The aqueous reduction-oxidation chemistry mechanism in the Hg version of RELMAP is applied only to the Hg$^{0}$ dissolved from the ambient air into the water droplet. Where significant concentrations of Hg$^{+2}$ from emissions exist in the ambient air, this Hg$^{+2}$ could be dissolved into the water droplet along with the Hg$^{0}$ and inhibit the scavenging of Hg$^{0}$. RELMAP simulation results described above indicate that Hg$^{+2}$ air concentrations are certainly lower than those for Hg$^{0}$ at the length scales of the RELMAP grid cells. However, the magnitude of the effect of ambient Hg$^{+2}$ on the Hg$^{0}$ oxidation scavenging is not yet well understood.

Another source of modeling uncertainty in aqueous chemistry relates to the fact that the aqueous chemical mechanisms were invoked only when and where precipitation was known to occur, and precipitation fields were only defined over land areas where precipitation observations were available. Significant wet transformation and removal of Hg may occur over oceanic areas where precipitation observations are not available, and it is possible that significant aqueous chemistry is occurring in nonprecipitating clouds.
Transport and diffusion. RELMAP simulates transport and diffusion only in the surface-based mixed layer. Vertical wind shear is small when the mixed layer is well defined, so under ideal conditions transport and diffusion are handled adequately. When the surface-based mixed layer is not well defined, however, vertical gradients in speed and/or direction of the wind may be present. These cannot be represented by the motion of individual Lagrangian puffs, whose layers remain vertically stacked. The most complete solution to the problem of vertical wind shear is the use of a Eulerian reference frame for numerical modeling. The EPA/AREAL has proposed development of a Toxics Linear Chemistry Model (TLCM) using the Eulerian reference frame of the RADM. Were this initiative to be adequately supported, the TLCM could be operational within 2 years.

Boundary fluxes of pollutants. Due to the RELMAP treatment of atmospheric pollutant loading as the combined effects of a population of discrete Lagrangian puffs and the long residence time of elemental Hg gas in the atmosphere, natural Hg emissions from the oceans and land surfaces cannot be explicitly modeled. The use of a Eulerian-type model would allow the definition of boundary fluxes of pollutants based on larger-scale model results or assumed background concentration levels.

Approach

The proper application of an environmental fate model requires specification of input data that describe and parameterize the environment being investigated. These data needs are discussed below.

Emissions inventory. Loadings of Hg introduced to the atmosphere from various sources, including coal-fired utilities, municipal waste incinerators, medical waste incinerators, and biomass burning, must be quantified and characterized. Knowledge of the oxidative state and physical form of the emitted Hg is important because these properties can influence the pattern of atmospheric dispersion and deposition. Knowledge of loadings of elemental, mercuric, and MeHg are desired. EPA/AREAL believes there is presently no adequate method for analyzing the species of Hg in emissions and, further, current stack sampling methods do not adequately characterize the chemical and physical form of Hg emissions as they manifest themselves on the regional scale. Chemical and physical transformations appear to be occurring in the exhaust flue and/or the local plume, and this creates a discrepancy between the Hg constituents measured in the stack and those measured in the atmosphere.

Wet and dry deposition fluxes. A spatial and temporal description of depositional loadings of elemental, mercuric, and MeHg is needed to drive aquatic fate models. While wet and dry fluxes may be measured at selected locations, a regional airshed model with local sources should be used with the observed data to more precisely understand loading patterns and distinguish among various local sources and regional and global background sources.

Mercury vapor concentrations and exchange rates. Elemental Hg in the air may undergo volatile exchange with concentrations in soil and water. This may provide a net source or sink to the ecosystem. Vapor concentrations in the air should be measured at selected monitoring locations; also, Hg vapor transport and reactions should be included in a regional airshed model. Experiments to quantify volatile exchange rates are needed.

Mercury plume chemistry. Physical and chemical reactions affecting Hg speciation in the plume must be described and quantified. These reactions are expected to affect the amount of Hg deposited locally in wetfall and the concentration of elemental Hg vapor that may exchange with the watershed. They may also help to explain the discrepancies in the chemical and physical form of Hg that often appear between stack gas measurements and ambient atmospheric measurements.

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