Appendix 7-5: Status of Atmospheric Deposition Measurement Studies

INTRODUCTION

As background information on the subject of mercury in the atmosphere, this appendix includes two documents prepared as part of the SFMSP research planning process.

The first document is a planning document prepared by DEP at about the time that it became apparent that the mercury budget of the Everglades is dominated by atmospheric inputs and that more emphasis within the program would have to be devoted to that sphere. This document was prepared to lay the background for state and federal budget requests to garner the support for this general element of the work.

The second document is a research plan for one of the more challenging aspects of the atmospheric portion of the work. Direct dry deposition of atmospheric constituents or pollutants can be a significant portion of deposition but measuring dry deposition is a challenge wherever attempted. The work proposed in the attachment forms the Basis for the Florida Everglades Dry Deposition Study, briefly discussed in the Ongoing Research section of Chapter 7.

MULTI-AGENCY ATMOSPHERIC MERUCRY STUDIES PROGRAM SOUTH FLORIDA MERCURY SCIENCE PROGRAM

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Understanding of the relative importance of the atmosphere as a pool and transport medium for natural and anthropogenically derived (both present-day and re-mobilization of earlier deposition) emissions of mercury has changed dramatically within the past decade. Prior to the development of 'clean' sampling and ultra-trace analytical procedures, concentrations of mercury in air, water and rain were commonly overestimated, often by two to three orders of magnitude (Fitzgerald 1986, 1989). Against this backdrop, anthropogenic sources of all types appeared small, with typical estimates of natural emissions accounting for 90 to 95 percent of total. More recent estimates of the global pools and fluxes of mercury suggest that natural emissions account for "*between 20 and 50 percent of the direct and indirect anthropogenic sources*" (Expert Panel, 1994). This, plus the finding that the accumulation of mercury in seepage lakes in remote areas may be largely attributed to atmospheric inputs (Watras et al., 1994), has focused attention beyond the problem of elevated mercury in fishes in these lakes to the potential importance of deposition processes, atmospheric transport and chemistry, and ultimately to sources of mercury to the atmosphere.

This view of the present situation is buttressed by studies of long-term trends of mercury in the environment by examination of cores of sediments and similar media. "*Considered individually, these methods are subject to much uncertainty. However, when considered as a whole they indicate that the total atmospheric mercury burden has increased since the beginning of the industrialized period by between a factor of two and five*." (Expert Panel, 1994). The significance of this increase is confounded by lack of uniformity, both temporally and geographically. For example, in some areas it has been shown that mercury deposition peaked between 1950 and 1970, at a level about three times present deposition rates. (Engstrom and Swain, 1995; Zillioux et al., 1993).

Are these broad trends applicable to Florida, a state lightly populated and industrialized prior to the present generation? What is the magnitude of deposition to Florida's waters and watersheds? What factors may influence this? To what extent can one view the problem of mercury in fish as driven by mercury from the atmosphere? These are questions posed to the state after the discovery of elevated levels of mercury in freshwater fish in 1989.

BACKGROUND & STATUS

As a potential contributor to the mercury problem in Florida, atmospheric processes are relevant on both local (within ca. 100 km) and global scales. That man's activities have resulted in a long term increase in the global background of mercury is now well accepted. The background is characterized by the predominance of Hg^o (typically 1-2 ng/m^3), a relatively non-reactive species with an atmospheric half-life of about one year,

averaging out to only slight gradients in atmospheric concentrations when away from cities, industrial centers or other, more poorly characterized, sources. Hg^o is slowly oxidized to a more reactive form (i.e., reactive gaseous mercury or RGM), which is then scavenged by rain and presumably contributes, proportionate to the historical trends, relatively uniformly to deposition in all regions, including south Florida. The several studies that have measured deposition rates at remote sites suggest that a typical background deposition rate approximates 10 $\mu g/m^2/y$.

There is also the potential that local factors, natural as well as anthropogenic, may augment the effect of the global background on south Florida. Approximately 4.5 million people live along a narrow coastal strip in the southeastern Florida counties of Dade, Broward and Palm Beach, and although not a heavily industrialized region mercury emissions are substantial relative to deposition. The magnitude of mercury emissions in the tri-county area of Dade, Broward and Palm Beach Counties are small relative to the background during the summer period of maximum deposition, but emissions of reactive mercury species are large relative to deposition. During the long warm season, regional weather is typically dominated by the Bermuda High, bringing steady southeasterly trade winds into Florida off the Atlantic Ocean. These winds bring with them mercury concentrations typical of the global background, pass over the urbanized corridor and out over the Everglades. During this same summer season the local meteorology is characterized by well-developed land breezes each day, which carry convective thunderstorm systems from the urban area and out over the Everglades. This peculiar weather pattern has the potential of exacerbating mercury deposition into the Everglades by two postulated mechanisms:

- The energetic mixing by these meteorological systems may enhance removal of mercury from the global background. One hypothesis is that vigorous scavenging by towering convective storm systems may more efficiently remove reactive gaseous mercury from the lower and free troposphere. Other hypotheses invoke increased rates of conversion of Hg^o to HgII by various mechanisms, such as reactions with ozone and free chlorine, in concert with sea-salt aerosols and anthropogenic particulate and gaseous species, or

- By forging a tight source-receptor relationship with local sources of mercury emissions (including, perhaps, more reactive forms), thereby focusing emissions from local sources out into the Everglades.

In 1990, the Florida Department of Environmental Protection (DEP) initiated a research planning process through the Center for Biomedical and Toxicological Research of Florida State University. Organized by Dr. Victor F. Lambou, a Technical Committee was assembled to assist the state in developing a response to the then-emerging findings of elevated mercury in freshwater fish. In its Interim Report dated 1992, the committee made a number of recommendations, among them that potential atmospheric sources of mercury be identified and measured.

In 1991, the Department issued a request for proposals for investigations of mercury in Florida. From this emerged three projects, all relating to potential sources of mercury into Florida, with particular focus on the Everglades region: an inventory of atmospheric emissions from within Florida, a study of long term trends of mercury accumulation in Everglades soils, and the last a pilot study of mercury in the atmosphere.

RESEARCH ELEMENTS - ATMOSPHERIC MERCURY STUDIES

The program of atmospheric research outlined herein was designed to be accomplished in stages, progressing from descriptive studies measuring the extent and magnitude of phenomena (Phase I), to process-oriented questions (Phase II) if atmospheric source were found to be plausibly significant to the Everglades system. Phase III studies, if indicated, would be to identify specific quantitative relationships between causative phenomena to determine the potential effectiveness of control strategies. The results and answers, as well as further questions, of each phase are given below.

Phase I - Mercury Emissions Inventory, Everglades Trends, and Deposition in Florida

The initial phase of any program of research must be descriptive, addressing questions of extent, magnitude, phenology, etc. The studies of gross emissions, temporal trends in mercury accumulation in Everglades soils, and atmospheric and deposition monitoring outlined in this sections represents this phase of the atmospheric mercury research program. The results of these studies have been very important in framing the way we now think of the problem.

Emissions

Florida typically is not thought of as an industrialized state, rather, the popular conception is one of beaches and sun. But even if this popular image remains, population growth over recent decades has changed the reality. The coastal ridge of south Florida now supports a dense urban population with its supporting infrastructure and economy. The emissions inventory, albeit based on approximations, suggests that emissions in Florida are significantly higher in areas of higher population and these are spatially arranged in a pattern that is plausibly significant to the Everglades.

The first funded of the studies called for in the Mercury Technical Committee Report, an inventory of emissions was based on published emission factors for various types of sources combined with the operating statistics of the specific sources in Florida. A report was completed in 1992 (KBN 1992), with significant revisions in 1994 (Baker and Roberson, 1994; KBN, 1994). This study showed that Florida, although not highly industrialized, contains significant sources of mercury to the atmosphere (Table 5-2). The average emissions per square kilometer for the tri-county areas of Dade, Broward and Palm Beach was 2.6 times greater than the state as a whole (0.481 kg/km^2 vs. 0.186 kg/ km^2). This may be due at least partly to a much higher population density in the tri-county area, which is more than three times the Florida average.

Historical Trends of Mercury Accumulation in the Everglades

At the time of the findings of elevated levels of mercury in Everglades fish, considerable opinion was expressed that it could be only a natural phenomenon as there was no evidence of pollution of the Everglades. Some sense of historical context was required in order to gain perspective on the problem. Therefore, the second study funded was of historical trends in mercury accumulation in the Everglades.

Forty-five cores of Everglades wetland soils were collected from Water Conservation Areas 1 (i.e., Loxahatchee National Wildlife Refuge), 2 and 3; and Everglades National Park. The cores were sectioned, dated by lead 210 and other historical markers, and sedimentation rates calculated for each stratum, which in combination with mercury analysis allowed for calculation of mercury accumulation rates. Considerable difficulty was encountered in extending a method developed for deep lake sediments to wetland soils, and variability among cores was a significant limitation on the accuracy and precision of estimates of determining mercury accumulation rates among various time horizons within the soil cores. As an overall average, however, mercury accumulation rates in the top 2 cm of soil were 4.9 times higher than the stratum representing the year 1900 (Table 10-2). Average accumulation rates ranged from 11 $\mu g/m^2/y$ ca. 1900 to 53 $\mu g/m^2/y$ ca. 1990 (Delfino et al., 1992; Rood et al., 1995).

Although limited in precision by the nature of Everglades soils and allowing for only the broadest analysis of spatial trends within the Everglades (generally increasing accumulation rates from south to north), the studies of Delfino and his students support the view that all terrestrial and aquatic systems have been subjected to increasing deposition driven, at least in part, by the increasing global background of mercury. The magnitude of the apparent trends in the Everglades suggests a rate of increase exceeding that which can be explained by the global increase alone. However, the question of what part overland transport may have played in the accumulation of Hg in Everglades soils has not been defined.

Atmospheric Deposition - Florida Atmospheric Mercury Study

The Florida Atmospheric Mercury Study (FAMS) was developed to measure long-term rates of atmospheric deposition of Hg in Florida. Using time-integrated, automated methods coupled with periodic intensive measurements, FAMS, since beginning its operational phase in 1993, has made direct measurements of wet-only and bulk deposition and inferential measurements of dry deposition (via measurements of total gaseous Hg {TGM} and ambient aerosol or particulate Hg). Coincident meteorology and trace elements also are measured at each site to provide insight into possible sources of Hg (e.g., marine vs. terrestrial, anthropogenic vs. crustal weathering). In addition to its primary goal of measuring regional rates of atmospheric deposition of Hg, the goals of FAMS include determining spatial patterns of deposition, particularly in south Florida where Hg in the Everglades has been identified as an important ecological issue, and whether these spatial patterns, coupled with evidence offered by elemental tracers, suggest possible sources contributing to Hg deposition impinging on the Everglades.

FAMS was begun by DEP in 1991 as a technology development and demonstration pilot study. The first FAMS monitoring site was set up in 1992 at Lake Barco near Gainesville, located in a remote ecological preserve, the site of a number of atmosphere/lake water interaction studies. Subsequently, Florida Power and Light Co. provided funding to continue operations at the L. Barco site and add four others in south Florida. With additional funding from DEP, EPA, FCG, and SFWMD the network was ultimately expanded to nine sites, two in northern and seven in southern Florida, including a marine background site at Crawl Key near Marathon (Fig. 10-2). Although the startup of the sites was staggered because of fiscal and logistical reasons, the project operated from early 1993 through 1996 to meet its goal of measuring 3-year-average annual deposition rates for each of the nine sites.

Interim results of FAMS through mid-1994 were presented at the Third International Symposium on Mercury as a Global Pollutant and published in the conference proceedings (Gill et al., 1995, Guentzel et al., 1995, Landing et al., 1995, Pollman et al., 1995)

Although FAMS continues to refine its estimates of long-term averages in deposition and spatial and temporal relationships, its preliminary information is very informative. Present-day deposition is seen to be at least double that typical of other rural sites where similar measurements have been made. Seasonality is strong, with ca. 85% of deposition coming in the summer months when the convective meteorology and southeasterly flows are dominant. Mainland deposition is significantly higher than the marine background sites and north Florida sites. Gradients among inland sites in south Florida, if significant at all, are subtle. Association of mercury with other atmospheric constituents is weak, with little apparent correlation with any source category.

Paradoxes

Despite much that is informative in these studies, puzzling inconsistencies remain:

FAMS estimates significantly increased deposition (vs. northern rural sites or marine background) yet the rates measured are less than half of recent sediment accumulation rates?

FAMS measurements suggest that total gaseous mercury (TGM) concentrations in the atmosphere are relatively constant throughout the year, yet the maximum deposition of HgII occurs in the summer. What processes are responsible for this disparity?

Limited information on gas and particulate phase mercury in the urban area suggest that concentrations are strongly elevated compared to FAMS sites.

Phase II - Source Testing, Ambient Monitoring, and Source-Receptor Model Validation: South Florida Atmospheric Mercury Monitoring Pilot Study (SoFAMMS)

Based on interim results of FAMS available in 1994 indicating that deposition of mercury in south Florida was approximately double (>20 $\mu g/m^2/y$) the levels generally observed at rural sites in more northern areas, plus limited evidence of unexpectedly high gas-phase and particulate levels of mercury in the nearby urban areas (Keeler et al., 1993; Dvonch and Keeler, 1995), a Phase II study was proposed to examine the potential contribution of local mercury emission sources in south Florida to the Everglades (Atkeson, 1994). The idea of a follow-on study to FAMS and other efforts was given serious consideration at a workshop held at EPA NERL in January, 1995, from which followed a formal plan of study developed as a collaboration between Dr. Roy Zweidinger, Mr. Robert Stevens (now with DEP) and Dr. Russell Bullock of the EPA National Exposure Research Laboratory, and Dr. Gerald Keeler of the University of Michigan Air Quality Laboratory.

The key ideas underpinning this effort were the observations of significantly increased deposition of mercury in the south Florida (FAMS), indications of high concentrations of mercury in the gas and particulate phases and in rain in the urban area (Dvonch and Keeler, 1995), and the apparent paradoxes posed by these two different

approaches to studying atmospheric mercury - one using long-term integrated samples to look at long-term averages and loadings, the other using high-frequency intensive sampling more suited to inference of source relationships or processes.

These and subsequent deliberations resulted in a coordinated, multi-disciplinary plan of research: South Florida Atmospheric Mercury Monitoring Pilot Study - Research Plan (Stevens et al., 1995). The proposed approach was a multi-agency pilot 30-day source and ambient air quality monitoring study initiated in the summer of 1995 and continuing through early 1997. Its purpose is to determine whether current measurement and modeling approaches are sufficiently robust to allow apportionment of the sources of atmospheric mercury to the Everglades.

The key tasks of this proposed monitoring/modeling study are:

1. Measure the chemical and physical forms of mercury emitted from 3 source types in south Florida (municipal solid waste incinerator, medical waste incinerator, cement kiln).

2. Measure emissions of other elements whose deposition may be correlated with that of mercury.

3. Obtain coincident meteorological measurement throughout the study domain.

4. Test differing modeling approaches potentially associating sources of certain characteristics with deposition in the near field (< 50 km).

A methods inter-comparison study designed to the FAMS monitoring results to that of this project. The project is considered a pilot study because:

1. The short duration (i.e. 30 days) of the ambient monitoring and source characterization.

2. The focus of the source characterization is limited to three (3) sources within a small geographical area.

The dispersion and receptor models will be modified and used, for the first time, to calculate the impact of Hg emissions of the sources on selected downwind receptors.

The field monitoring and testing phase of the SoFAMM Study was successfully conducted during August and early September of 1995. Sample analysis continues as of the date of this report. Data analysis and modeling will be completed in mid-1997.

The conclusions of SoFAMMS, and what new understanding emerges from this study, must await its completion. Nonetheless, we may envision three scenarios:

1. The study may fail to meet its primary objectives because of inadequacies in available techniques for measuring the relevant species of mercury in the atmosphere, or the various modeling regimes applied to the data may be inadequate to account for the transport and fate of mercury from the sources to the receptor sites. In this case further consideration of source-receptor relationships would need await advances in measurement techniques.

2. The study may succeed in its technical objectives, to measure and model the transport and deposition of mercury, but the magnitude of the association may be so small as to be of negligible environmental or policy significance. Should this conclusion obtain, there would be little justification for further consideration of local source impacts on the Everglades.

3. The study may meet its technical objectives and conclude that present methods and models yield strong, robust associations between emission and deposition, suggesting that emissions within south Florida may be quantitatively significant to the problem of mercury in fish in the Everglades.

Phase III - Quantitative Regional Transport and Effects Model

Should the third outcome of SoFAMMS obtain (see above), then it should be followed by a more comprehensive investigation of south Florida regional Hg emissions, transport and deposition. This would involve a more extensive, multi-year program of source testing and chemical and meteorological monitoring to precisely estimate the magnitude of the combined regional effect of many and varied sources on depositional loadings of mercury into the Everglades.

(note: This phase of the work has not been funded but remains under discussion between DEP and USEPA. Elements of a project such as this are included in the EPA National Merucry Research Strategy. The decision to pursue this regional study await results of the 'mercury super site' monitoring that began in May, 2000.)

Table A7-5-1. Estimated Average Total Mercury Emissions in Florida for 1990

Category	Hg Emissions (lb.)	Percent of Total	
ANTHROPOGENIC			
MSW Combustion	9,152	17.0	[1]
Electric Utility Industry	3,100	5.6	[2]
Medical Waste Incineration	3,400	6.3	[3]
Sugar Cane Processing	296	0.5	
Pulp and Paper	0	0.0	
Cement Manufacturing	102	0.2	
Chlor-Alkalai Manufacturing	0	0.0	
Other Fuel Burning	1,050	1.9	
Paint Application	6,980	13.0	
Electrical Apparatus	3,703	6.9	
Dental Preparation	50	0.1	
Laboratory Use	147	0.3	
Transportation - Diesel	405	0.8	
- Gasoline	429	0.8	
- Aviation Fuel	7	.01	
Open Burning	404	0.7	
Sewage Sludge Disposal	123	0.2	
TOTAL ANTHROPOGENIC	29,348	54.5	
NATURAL			
Soil Degassing	24,440	45.4	
Forest/Natural Fires	79	0.1	
TOTAL NATURAL	24,519	45.5	
TOTAL	53,867		

Source: KBN, 1992, as revised KBN 1993, FCG 1994

1. Recent data indicate that emissions have declined since 1990 because of removal of Hg from commercial products, especially batteries.

2. Revised on basis of EPA tests through 1992

3. Revised on the basis of DOE and EPRI tests through 1994

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MEASUREMENT OF THE DRY DEPOSITION AND AIR-SURFACE EXCHANGE OF MERCURY TO THE FLORIDA EVERGLADES

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PROPOSAL SUMMARY

The Florida Everglades appear to receive among the highest loading rates of atmospheric mercury in the U.S., based on recent wet deposition measurements. Sediment core data from the area indicates that the long-term and recent loading rates are higher than can be accounted for by measured wet deposition alone. Depending on the source proximity, dry deposition typically contributes 25-50 percent of the total atmospheric load of pollutants to ecosystems. Recent data from forests in Tennessee, Vermont and Sweden suggest that dry deposition of mercury may exceed its wet deposition by as much as a factor of two. Because new data from the 1995 SoFAMMS suggest that the largest source(s) of atmospheric mercury to the Everglades may be local in origin, it is imperative to develop a complete understanding of dry deposition in this region to assess the effects of these local sources on the dry deposition input to the Florida Everglades.

Measurement of the dry deposition of mercury and other semi-volatile organic compounds (SOCs) is non-trivial. Mercury and other SOCs are found in both the particulate and vapor phases, with measurement of each phase presenting its own problems. The use of surrogate surfaces is one approach, which has been used to obtain a direct measurement of the dry deposition of trace metals to the water surface. Until

recently, these methods could not be used to estimate the dry deposition of mercury and other SOCs because of interferences with the greased surfaces typically used with surrogate surfaces and due to contamination by the vapor phases of these species. Recently, analysis and measurement techniques for the estimation particulate and vapor phase dry deposition of mercury have been developed by the University of Michigan Air Quality Laboratory (UMAQL) through EPA Grant #CR 822054-01 entitled *"Dry Deposition of Mercury and Other Compounds to Natural Water Surfaces"* (Gerald J. Keeler, PI). These measurement methods include the use of a new surrogate water surface. Comparison of the water surface with traditional greased surfaces has shown good agreement for non-volatile trace metals (Glinsorn and Keeler, unpublished). The use of the water surface provides an approach to obtaining an estimate of total mercury (vapor plus particulate) dry deposition. Tests by the UMAQL have shown that significant vapor-phase elemental mercury is not taken up by the water surface. Thus, a measure of the reactive vapor-phase mercury deposition can then be achieved through a comparison of the total Hg in the water surface with that found on the greased surfaces, which are only efficient at collection of particulate matter.

The unique vegetation that is native to the Florida Everglades provides an additional challenge to the measurement of dry deposition of mercury to this ecosystem. While a portion of the dry deposition of mercury to the Everglades occurs via direct deposition to the water surface, an additional input of mercury to this aquatic ecosystem likely occurs via deposition of mercury to Everglades vegetation, with eventual delivery to the water surface via throughfall. This throughfall deposition will occur when the mercury dry deposited to the vegetative surfaces is washed off the surfaces and delivered to the water surface during precipitation events.

By virtue of the volatility of its compounds, mercury is unique among the trace metals in its environmental cycling. Once deposited, the behavior of mercury more closely matches that of certain organic compounds than typical metals. In recent years, we have begun to understand the ability of Hg to be emitted (or re-emitted) from a variety of surface types (biota, soils and water). These emissions can significantly influence mercury's persistence in these ecosystems. Mercury emissions have been reported from water surfaces in both marine and freshwater systems (e.g., Fitzgerald *et al.* 1994; Lindberg *et al.* 1996). The mechanism for mercury emission from water (often termed evasion) may be biologically mediatiated but recent evidence suggests an important role for the direct photochemical reduction of divalent mercury (Hg^{2+}) to elemental mercury vapor (Hg^0) (Amyot *et al.,* 1994; Xiao *et al.,* 1995) with its subsequent evasion.

To date, several different techniques have been employed to estimate the evasion of mercury from water surfaces. Early estimates of mercury evasion have employed stagnant film models (a two-layer gas transfer approach) with measurements (or estimates) of dissolved gaseous mercury (DGM) (e.g., Fitzgerald *et al.,* 1994). While these methods do provide some insight into the potential magnitude of mercury evasion, they do not represent a direct "in situ" measurement of evasion. Recently, direct methods for quantifying mercury evasion were developed by Dr. Steven Lindberg (ORNL). One such method employs a dynamic flux "chamber". While this technique offers a direct measurement of evasion, it represents the flux over a small surface area (approximately 1 m^2), which may not be entirely representative of the surface being measured. Further, the presence of the chamber alters the character of the atmospheric turbulence over the surface in question, thus potentially altering the nature of the air-surface exchange dynamics. A second method, that of the modified Bowen-ratio (MBR) technique, has

been employed by Dr. Lindberg and Dr. Tilden P. Meyers of the NOAA Atmospheric Turbulence and Diffusion Division (NOAA-ATDD) in Oak Ridge, TN. The MBR approach requires that both the fluxes and gradients of at least one passive scalar can be measured in order to directly compute the transfer coefficient, *K*. Assuming that this transfer coefficient is applicable for all passive scalars, the empirically derived transfer coefficient can then be used to estimate the surface fluxes of other trace species (such as vapor phase mercury) for which direct flux measurements may not be possible. Initial application of the MBR technique over a boreal forest lake in Sweden has proven highly successful (Lindberg *et al.*, 1995). The method was also used by the UMAQL over an inland lake in northern Michigan during the 1996 Burt Lake Atmospheric Deposition Experiment (BLADE). The UMAQL also utilized the chamber technique during the BLADE to begin to understand the limitations and uncertainties of these techniques.

Until now, process studies related to the cycling of mercury at water surfaces have generally focused separately on either the deposition of particulate and vapor phase mercury to water surfaces or the evasion of mercury from water surfaces. This project proposes to perform a complete air-surface exchange study (both deposition and evasion) at locations (at least two) within the Florida Everglades. The primary focus of this work will be to obtain an understanding of the primary mechanisms of the dry deposition of mercury species in the Florida Everglades and to obtain a preliminary estimate of the rates of air-surface exchange of mercury within this ecosystem. In the first phase of this project, measurement techniques will be developed and tested during a field campaign scheduled for the late Fall 1998 or Winter 1999. Preliminary estimates of the exchange rates of mercury species in the Florida Everglades will be obtained. A second field study would follow in the wet season during the Summer 1999. This second field study will allow further testing of the measurement techniques and for a comparison of the mercury deposition and air-surface exchange rates during the summer (wet) and winter (dry) seasons.

I. OBJECTIVES

There are three overall objectives to this proposed project.

1. Develop new surrogate surface, and refine existing, measurement techniques required in the quantification of the air-surface exchange of mercury species to the Florida Everglades. To better understand the impact of local anthropogenic Hg sources on the Florida Everglades, a complete understanding of the processes associated with the air-surface exchange of mercury in the Everglades is necessary. The unique surface characteristics associated with the Florida Everglades (a combination of water, sawgrass and cattails), requires that a new approach to examining air-surface exchange be used. The first phase of this study will focus on the development and refinement of new and existing surrogate surface, and other measurement techniques necessary for the quantification of the air-surface exchange of several mercury species {Hg^0, Hg^{2+}, Hg(p)}.
2. Use the techniques developed in Objective #1 to quantify the rates of, and understand the primary mechanisms associated with, the air-surface exchange of mercury species to the Florida Everglades. The newly developed/refined techniques will be tested during a field campaign scheduled for late Fall/Winter 1998/99. During this field study, efforts will be made to determine which of the new techniques provide the most reliable estimates of the air-surface exchange of mercury. Insofar as results

allow, preliminary estimates of the exchange rates will be determined for the different processes involved in the air-surface exchange of mercury species in the Florida Everglades.

3. Investigate the seasonal variability associated with the air-surface exchange of mercury species in the Florida Everglades. Building upon the lessons learned during the late Fall/Winter 1998/99 field study, a second field study will be conducted during the Summer 1999. The performance of multiple field campaigns at the same location will allow us to investigate the potential differences in the air-water exchange of mercury species during the dry (Fall/Winter) and wet (July) seasons in the Florida Everglades. The factors to be investigated include variations in solar insolation, water temperature and microbial activity. Furthermore, seasonal differences in the air-surface exchange of mercury to the Florida Everglades may result due to seasonal differences in rainfall across this area, and thus result in differences in the relative partitioning between dry and wet deposition.

II. EXPECTED RESULTS OR BENEFITS

This project will lead to a better understanding of air-water surface exchange processes for mercury in the Florida Everglades. The project will provide one of the first attempts to look at the complete air-water exchange process, by including simultaneous measurements of ambient mercury concentrations (particulate and vapor phase (including both Hg^0 and Hg^{2+}), deposition (wet and dry) of mercury to the water surface, surface water concentrations of mercury (DGM, RM, TM) and evasion of Hg^0 mercury from the water surface. The new RGM measurement technologies include modified Tekran and automated wet-denuder systems. Further, by conducting two field intensives throughout the year, we will obtain information on the seasonal differences in the air-water exchange processes involving mercury and other trace species.

Finally, based on the preliminary results of the 1995 South Florida Atmospheric Mercury Monitoring Study (SoFAMMS), a more extensive study has been suggested. The "refined" SoFAMMS would look more completely at the effects of mercury emissions from the heavily developed southeast coast of Florida on the deposition of mercury in the Florida Everglades. The lessons learned from the process studies suggested in this proposal will be used in the planning of deposition measurements to be made during the proposed future SoFAMMS.

III. TECHNICAL APPROACH

The overall objectives presented earlier in this document will be accomplished through a joint effort between the UMAQL and the ORNL. These two groups are uniquely qualified to perform these tasks, and thus it is felt that the established working relationship between these groups will benefit the State of Florida Department of Environmental Protection by ensuring that quality and scientifically credible conclusions will result from this collaborative effort. The approaches used to meet the aforementioned objectives are as follows:

Task 1:

Develop new, and refine existing, measurement techniques necessary for the quantification of the dry deposition and air-surface exchange of mercury species to the Florida Everglades.

As noted earlier, the unique surface characteristics (a combination of water, sawgrass and cattails) found in the Florida Everglades will require new approaches to examining dry deposition and air-surface exchange of mercury species to this particular ecosystem be developed and implemented. These approaches will require a blending of new and existing dry deposition and air-surface exchange measurement methods. A full description of the measurements to be employed in this effort will be detailed in Task 2.

It is currently expected that three new measurement techniques will be developed for use in this proposed study. These techniques will be tested during the Fall/Winter 1998/99 field study, refined and then employed in subsequent field efforts associated with this project. These "new" techniques involve the following:

1. Dry deposition to the Everglades vegetation (and the resultant delivery to the air-water interface via throughfall).

2. Ambient measurements of divalent vapor phase mercury (Hg^{2+}).

3. Uptake of mercury by dew.

1.1 Report on development and validation experiments performed.

Provide a detailed report on the development, testing, and validation of the various methods for sampling divalent vapor phase mercury (Hg^{2+}) and measuring dry deposition mercury.

1.2 Dry deposition to the Everglades vegetation (and delivery to the air-water interface via throughfall)

The unique vegetative surfaces that are indigenous to the Florida Everglades pose an interesting challenge as to how to best measure the dry deposition of mercury species to these surfaces (via impaction and gravitational settling) and then the eventual delivery of these species to the air-water interface. To address this problem, the UMAQL will develop several prototype throughfall sampling systems, which will be tested during the first proposed field study in Fall/Winter 1998/99. It is anticipated that the dry deposition/throughfall sampling systems will consist of collection surfaces that will be located at the base of the vegetation. These surfaces will be designed such that they will capture throughfall water resulting from natural precipitation. It is felt that by placing these receptors at the base of the vegetation, direct dry deposition to the collection surfaces will be limited. The collection surfaces will contain a drainage spout that will be used to direct the collected sample into Teflon bottles for transport to analytical facilities. Following analysis, the concentration of throughfall samples can be compared to precipitation samples taken above the vegetation to determine the amount of mercury in the throughfall which results from the washing of dry deposited material that was located on the vegetative surfaces. From the lessons learned during the Fall/Winter 1998/99 and

Summer 1999 field study, a throughfall collection method will be chosen (or modified) and used in subsequent studies.

1.3 Ambient measurements of divalent vapor phase mercury (Hg^{2+})

Recent evidence indicates that Hg^{2+} vapor may represent a significant fraction of the total vapor phase mercury burden in the atmosphere (Prestbo and Bloom, 1991). As a result, this study will employ one of the newly developed techniques, either a refluxing mist chamber (Stratton and Lindberg, 1995) and/or the wet annular denuder, for the measurement of ambient Hg^{2+} vapor. In addition to using this new technique for ambient measurements, it is anticipated that the mist chambers will be employed to determine the feasibility of the measurement of vertical gradients of Hg^{2+} vapor above the Everglades vegetation. These gradients will be used in conjunction with micrometeorological measurements described below in an attempt to estimate the air-surface exchange of Hg^{2+} in the Everglades.

1.4 Uptake of Mercury Species by Dew

The nocturnal formation of dew on the surfaces of the vegetative surfaces with the Florida Everglades is likely to greatly alter the deposition surface characteristics of this vegetation. Preliminary measurements of dew chemistry in S. Florida will be made during this project in an effort not only to estimate the magnitude of mercury species concentrations in the dew, but also to study the processes associated with the uptake of mercury by dew drops. Potential pollutant uptake mechanisms include the scouring of mercury species from vegetation surfaces by the formed dew drops and/or the direct deposition of mercury species to the dew drops themselves. A 4' x 4' Teflon deposition surface will be employed to collect the dew samples during the study. The surface is constructed to allow it to be bent in half, forming a channel at the centerline of the surface. The collected dew sample runs into the channel, with residual sample removed from the surface via a specially designed Teflon squeegee. The surface is then tilted such that the collected dew sample flows down the channel and into a Teflon collection bottle. The UMAQL has utilized the all-Teflon dew sampler effectively in Michigan and have proven it reliable for Hg and trace element sampling. Field blanks taken before and after each sample give blanks that are less than 10% of the typical dew concentration.

Task 2:

Use the techniques developed or refined in Task 1, to quantify the rates of, and understand the primary mechanisms associated with, the dry deposition and air-surface exchange of mercury species to the Florida Everglades.

The newly developed/refined techniques will be tested during a field campaign scheduled for Fall/Winter 1998/99. The site to be used for the study is yet to be determined. A potential site would be located midway between water monitoring stations S-6 and S-7 (Water Conservation Area 2). Another potential site was visited during the July 1997 ACME intensive and the site at 3A-15 would also prove to be a suitable site, but the lack of power at that location may prohibit its use. During the field study, efforts will be made to determine which of the new techniques provide the most reliable estimates of the various components of dry deposition and air-surface exchange of mercury species in the Florida Everglades. Inasmuch as results allow, preliminary estimates of the exchange rates will be determined for the different processes involved in

the dry deposition and air-surface exchange of mercury species in the Florida Everglades. **Table A-7-5-2** lists the measurements that are currently planned, as well as the expected frequency of these measurements.

Table A-7-5-2. Planned measurements and frequencies for the 1998/99 Everglades Intensives.

Measurement	Frequency
Ambient	
Particulate Hg and trace elements	Two 12-hour samples per day
Total Vapor Phase Hg	Continuous (15 minute average)
Vapor phase Hg^{2+} -Mist Chamber and wet annular denuder	To be determined (several per day)
Dry Deposition	
Aerodynamic water surface	Two 12-hour samples per day
Vegetation Throughfall	Event samples
Flux	
Hg^0 gradient and Hg^{2+} gradient - mist chambers and/or automated wet annular denuders or modified Tekran analyzer.	Continuous (15 minute averages) To be determined (several per day)
Wet deposition	Event samples
Dew	8-12 Hour overnight
Meteorological Variables	Continuous

The measurements listed in **Table A-7-5-2** will be made following well-defined protocols. These include the measurement of aerosol trace elements and mercury. The surrogate water surface was developed by the UMAQL and was tested during the 1995 SoFAMMS. Total vapor phase mercury measurements will be made using a Tekran Continuous Hg Analyzer. Continuous sampling intervals of 15-30 minutes will be obtained with the Tekran during the sampling campaigns. Wet deposition measurements will be performed on an event basis using the manual methods utilized during the 1995 SoFAMMS (Dvonch *et al*., 1997). Measurements of total and reactive Hg, and trace elements by ICP-MS will be made on all precipitation and vegetative throughfall samples.

A full suite of meteorological variables will be measured continuously during the field intensives. The variables to be measured include global solar radiation, net radiation, ambient temperature/relative humidity, temperature/water vapor/CO_2 gradient above the vegetation. The meteorological variables will be measured to obtain a general characterization of the micrometeorological conditions in the turbulent surface layer above the vegetation. The measurements will also be used in the estimation of vapor phase mercury deposition and evasion.

The measurements described above will take place during two-week intensive sampling periods. The length of about two weeks has been chosen to allow us to

investigate mercury deposition and air-surface exchange processes over a variety of synoptic and environmental conditions. Given the stochastic nature of turbulence, we feel that it would be difficult to characterize "typical" air-water exchange characteristics using a shorter sampling period.

Task 3:

Investigate the seasonal variability associated with the air-surface exchange of mercury species in the Florida Everglades.

Field intensives are proposed to take place during the Fall/Winter 1998/99 and the following Summer 1999. The performance of multiple field campaigns at the same location will allow us to investigate the potential differences in the air-water exchange of mercury species during the wet and dry seasons in the Florida Everglades. The factors that may lead to differences in the exchange rates include variations in solar insolation, water temperature and microbial activity. Furthermore, seasonal differences in rainfall across this area may result in differences in the relative partitioning between dry and wet deposition.

As noted, several intensive sampling campaigns will be performed during the coarse of the year. The UMAQL has observed, in our studies in the Great Lakes, that a strong diurnal cycle in the evasion of mercury from surface waters can be seen with a peak occurring near solar maximum. This has also been observed by other researchers such as Amyot *et al.* (1994) and Lindberg *et al.* (1995). It is hypothesized that this dependence on solar irradiance can be seen not only in the diurnal pattern of mercury evasion from surface waters, but it will likely be evident when comparing seasonal differences in the mercury evasion from surface waters. In addition to the differing solar irradiance characteristics from season to season, differences in average air and water temperatures between the seasons will likely lead to different over water stabilities. These stabilities no doubt play a role in the nature of turbulence over the Everglades surface, thus affecting the evasion of mercury. This study will provide the first look at such seasonal differences.

The Fall/Winter 1998/99 field study will build upon lessons learned during the July 1999 field study. Modifications will be made to sampling equipment/strategies as is deemed necessary. Details of these modifications will be discussed in detail with the Florida Department of Environmental Protection prior to the commencement of the 1998/99 field studies.

IV. QUALITY ASSURANCE

Quality Organizational Structure

The PI of the project, G.J. Keeler, will be responsible for establishing and maintaining communication with the Florida DEP Project Officer. The PI will also be responsible for insuring that the all aspects of this project are carried out in accordance with the quality assurance guidelines deemed necessary to insure the highest possible quality of data.

Quality Assurance Activities

The UMAQL and the ORNL have collaborated on mercury research since 1992. Class 100 clean air facilities for trace level mercury determinations are utilized and samples are continually exchanged between the two groups for QA tests. These exchanges will continue during the proposed project to ensure that analytic accuracy is maintained. Both laboratories recently participated in an international mercury intercomparison, with excellent (and comparable) results (Bloom *et al.,* 1995).

Trace element protocols will be employed in all facets of laboratory analysis (Landis and Keeler, 1997; Rossman and Barres, 1989; Fitzgerald and Watras, 1989; Nriagu, 1990).

FACILITIES

Laboratory Facilities

The UMAQL operates two state-of-the-art clean laboratories (Class 100). The University of Michigan facility is used for ultra-trace element analysis of environmental samples and is a dedicated facility for environmental studies requiring low-level trace element quantification. The laboratory has its own ultra-high purity water purification system and employs a rigorous 30-step bottle and sample container cleaning procedure. This extensive process utilizes only ultra-pure acids and water throughout. All drying of bottles and containers is performed in the clean room. As noted, trace element protocols are employed in all facets of laboratory analysis (Landis and Keeler, 1997; Rossman and Barres, 1989; Fitzgerald and Watras, 1989; Nriagu, 1990).

Computer Facilities

State-of-the-art computer resources are available within the UMAQL and the University of Michigan. Presently, a SUN SPARCstation/10 is utilized for ingestion, display, analysis and archival of real-time meteorological data from the National Weather Service and the National Oceanic and Atmospheric Administration. This computer is housed in the Space Physics Research Laboratory. The UMAQL houses one SUN SPARCstation IPC (with one gigabyte local storage capacity, plus a 750 megabyte external storage device), one SUN SPARCstation/20 (with a 3.9 gigabyte external storage device) and one Sun UltraSPARC Workstation (with a 2 gigabyte hard drive, 128 megabyte RAM and a 167 megahertz processor). Finally, the UMAQL owns an Exabyte 8505 High Density tape drive, which will be used for data storage and retrieval.

Fiber-optic ethernet connections allow the rapid transfer of data across the School of Public Health and the University of Michigan computer network. The School of Public Health InfoTech Network provides AFS cells for data storage as needed. The UMAQL also houses a large number of Pentium-class and 486 class microcomputers for data manipulation, word processing, statistical analysis, and graphics.

In addition, the University is also networked via NSFNET to Cray supercomputers at the National Center for Atmospheric Research and at the University of California at San Diego. The UMAQL is networked via Internet to virtually all communications worldwide. The MERIT network allows instant access to our data files through local access in most Michigan cities. The NSFNET Ethernet connection allows very high-

speed communications from University of Michigan computers to other sites throughout the world. Additional electronic communication paths are available to the UMAQL and the SPRL through a wide variety of commercial networks.

Software Library

The UMAQL software library contains all of the necessary tools to carry out the tasks as described in Section III. Basic statistical analyses will be carried out using the SAS Statistical Software Package (SAS Institute, Incorporated, Cary, NC). This package will allow for sophisticated multivariate correlation analyses, as well as the use of various hypothesis testing approaches. The UMAQL software library also contains the most recent version of the Regional Atmospheric Modeling System (RAMS), Version 3B. Further, a Lagrangian particle dispersion model and air mass trajectory model (HY-SPLIT) are available to assist any source apportionment that may be used as part of this project.

The University of Michigan has a site license for the NCAR Graphic software package, which will allow for the detailed graphical presentation of the RAMS model output. Also, advanced data display software available at the University of Michigan will allow for the presentation of transport simulations in an animated, three dimensional format.

PERSONNEL

Gerald J. Keeler, Ph.D. presently holds an appointment as an Associate Professor in the Dept. of Environmental and Industrial Health as well as in the College of Engineering in the Dept. of Atmospheric, Oceanic, and Space Sciences, at the University of Michigan in Ann Arbor. He started the University of Michigan Air Quality Laboratory (UMAQL) in 1990. He has extensive experience in planning, conducting, and managing large field studies aimed at understanding air quality and environmental problems. His focus has been on the measurement and modeling of atmospheric aerosols including acids and associated trace elements. He has been involved in research and monitoring programs in all parts of the United States and Canada. In 1991, he was the Principal Investigator for the Lake Michigan Urban Air Toxics Study jointly performed by the UMAQL and EPA-NERL. Since 1991, Dr. Keeler has been a leader in atmospheric mercury research and methods development. His group has carried out the most extensive field studies of atmospheric mercury and trace element transport and deposition in the Great Lakes region. Most recently, he designed, organized and managed the 1995 South Florida Atmospheric Mercury Monitoring Study (SoFAMMS). Dr. Keeler will serve as a PI for this project. He will be responsible for the coordination of wet and dry deposition measurements associated with the project and perform data analysis and manuscript preparation.

Frank J. Marsik, Ph. D., currently holds an appointment as a Post-doctoral Research Fellow in the Department of Environmental and Industrial Health at the University of Michigan in Ann Arbor. His doctoral research focused on the micrometeorological aspects of earth-atmosphere turbulent exchange processes. He has extensive experience in planning and conducting micrometeorological support for various air quality field programs. Among the projects in which Dr. Marsik has participated are the 1990 Lake Michigan Ozone Pilot Study, the 1991 Lake Michigan Urban Air Toxics Study, as well as the 1992 and 1993 forest-atmosphere exchange measurement campaigns associated with

the EPA's Southern Oxidants Study. He has most recently been working with scientists at NOAA's Atmospheric Turbulence and Diffusion Division on methods development related to surface mercury flux measurements. Dr. Marsik will be responsible for overall coordination of the meteorological measurements associated with the project and participate in report writing and manuscript preparation.

Steven E. Lindberg, Ph.D., Is a senior research scientist at the Oak Ridge National Laboratory (ORNLl). He is the leader of the atmospheric and biogeochemical cycling group in the ORNL's environmental sciences division. Under his leadership, ORNL has acquired considerable expertise in the research and development of mercury flux measurement methods. Many of the recent advances in the study of airborne mercury fluxes and speciation have been made at the ORNL under Dr. Lindberg's direction. These developments include use of the modified Bowen ratio approach, mist chambers for gas-phase mercury speciation studies and an all-Teflon dynamic flux chamber. With colleagues at the NOAA atmospheric turbulence diffusion division, Dr. Lindberg has developed, modified, and tested different methods to measure the atmosphere-surface exchange of mercury over soils, vegetation and waters. Dr. Lindberg has been an author or co-author for over 150 papers. An unquestioned leader in the field of the biogeochemical cycling of mercury in the environment, he has won numerous awards for his leadership in this field. Dr. Lindberg will be responsible for the measurements associated with vapor-phase mercury evasion from the lake surface and will serve as a co-investigator on the project.

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