

CHAPTER

Recent Trends in Mercury Emissions, Deposition, and Biota in the Florida Everglades: A Monitoring and Modeling Analysis

Thomas D. Atkeson¹, Curtis D. Pollman², and Donald M. Axelrad¹

¹Florida Department of Environmental Protection, MS 6540, 2600 Blair Stone Road Tallahassee, FL 32399-2400 USA

²Tetra Tech, Inc., Suite 301, 401 W. University Ave., Gainesville, Florida 32601-5280 USA

Abstract: In 1989, monitoring by Florida state agencies revealed that mercury in largemouth bass from the Everglades averaged over 2 mg/kg – well above the Florida Department of Health advisory limit of 0.5 mg/kg for limited consumption of fish. Long-term trend monitoring indicates peak mercury concentrations in largemouth bass occurred in the mid-1990's, and by 1999 declining trends were apparent throughout Florida. Recent data indicate mercury declines in fish from portions of the Everglades of ca. 80%. Similar declines in mercury in wading birds in the Everglades have been reported. Because atmospheric deposition is the major source of mercury to the Everglades, one hypothesis that explains the observed biota mercury concentration trends links the declines in mercury in biota to declines in local emissions of mercury. This study examines whether this hypothesis is supported by the extant data or whether the apparent trends in biota are more appropriately related to other factors or perturbations. Several fundamental questions are addressed to test this hypothesis: (1) are the reported trends of mercury in biota robust and self-consistent; (2) are there concomitant trends in local emissions of mercury consistent with mercury declines in biota; and (3) are changes in atmospheric deposition fluxes of mercury consistent with changes in local emissions?

With the discovery in 1989 of widespread, severe contamination of biota by mercury in the Florida Everglades, the Florida Department of Environmental Protection and its many collaborators mounted a sustained program of monitoring, modeling and research to plumb the causes of this problem and propose solutions. This analysis describes the 15-year trend records and reconstructions developed to put the research findings in historical context, whereas the process-level research findings are reported elsewhere. At the time these studies began neither the causes of this problem were apparent nor was there any expectation among the scientists that any would live to see the fruits of their labors – *viz.*, a significant decline in mercury in Everglades biota.

However, and most gratifyingly, beginning mid-decade of the 1990's and continuing into the new millennium, progressive, statistically significant declines in mercury concentrations have been observed in both largemouth bass and great egret nestlings at a number of sites located throughout the Everglades (Pollman et al., 2002; Frederick et al., 2001). It was not until later that retrospective studies determined that marked declines in local emissions and deposition of mercury (RMB, 2002; Husar and

Husar, 2002) from the major point emissions sources in southern Florida antedated the declines in emissions and deposition.

Atmospheric sources of wet and dry deposition are now accepted as the major sources of mercury to the Everglades (Stober et al., 2001), and because local emissions have been inferred to be the predominant source of mercury deposited in south Florida rainfall, including the Everglades (Dvonch et al., 1999), the question arises whether the observed declines in biota mercury concentrations can be related to declines in local emissions.

This chapter reviews the existing data on mercury emissions, deposition, and biota trends in south Florida in order to address this question. Much of this discussion is based on work previously published by Pollman et al. (2002) and Pollman and Porcella (2003), but extends that work by including more recently available, longer time series for biota concentrations, as well as incorporating new analyses on wet deposition trends of mercury and some exploratory model hindcasting to examine the relationship between emissions and deposition, and aquatic biota response.

This analysis integrates information from numerous studies to evaluate the causal relationship between mercury emissions, deposition and biotic response in the Florida Everglades. We began first with an examination of the recent trends in both mercury emissions and, as a surrogate to test the robustness of the emissions trends, mercury use. The mercury emissions and usage trends data were compiled by RMB Consulting & Research (RMB; 2002) and Husar and Husar (2002), respectively, for the major sources of mercury emissions in south Florida including municipal waste combustion (MWC) and medical waste incineration (MWI) facilities. These results indicate that large reductions in emissions (approximately 90% relative to peak emissions), occurring ca. 1991.

Second, we statistically analyzed wet deposition fluxes for mercury from November 1993 through December 2002 for samples collected in Everglades National Park to determine whether these trends can be related to changes in the atmospheric signal, or are related to changes in rainfall patterns. Although the monitoring period for wet deposition began well after the largest fraction of the reductions in local emissions had occurred, the wet deposition signal still showed a significant decline (ca. 25%; $p = 0.0413$) that agrees reasonably well with the emissions declines during the same period.

Third, we compare the biota trends to examine whether the timing and magnitude of changes in largemouth bass mercury observed in the Everglades are consistent with predicted changes produced by the changing deposition trajectory. These results suggest that the biota changes are indeed consistent with the estimated declines in local emissions and deposition, although additional analyses to test other hypotheses should be conducted before more definitive conclusions are reached.

1.1 Trends in Mercury Emissions

Two fundamentally different types of analyses have been conducted to reconstruct recent trends of mercury emissions in south Florida. The first was a direct approach where a historical emissions inventory was compiled for the period 1980 to 2000 for southeastern Florida (i.e. Broward, Dade and Palm Beach Counties (RMB, 2002). Emissions were estimated from plant operational data and emission factors typical for the source under consideration. These three counties were selected as the region containing sources most likely to be important local contributors to mercury deposition in the Everglades and south Florida. The second approach was an inferential or indirect approach, where the trend in local emissions was inferred by reconstructing a mass balance on the flows of mercury ascribed to various use categories or major economic sectors (Husar and Husar, 2002). This latter analysis first focused on mercury use on a national scale, beginning in 1850 and continuing to 2000, then reduced the scale of analysis to the state level for Florida, and finally concluded with a regional analysis for Broward, Dade, and Palm Beach counties in southeast Florida for the period 1950 through 2000.

The emissions estimates compiled by RMB (2002) indicated very large changes occurred between 1980-2000 as a function of the major combustion sources in south Florida (power generation, sugar industry, incineration of municipal and medical wastes; Figure 1). Total emissions were quite low between 1980 and 1982, and then increased in 1983 by 3.5 times above 1982 levels as both municipal waste combustors (MWC) and medical waste incinerators (MWI) came on line. Local emissions continued to increase through the 1980's until 1991, when a peak emission flux of nearly 3,100 kg/yr of total mercury was estimated. Throughout the peak emission period of 1983-1991, the predominant local mercury emissions source was medical waste incinerators (MWI's, 47 to 76% of the total); when combined with municipal waste combustors (MWC's), these two sources comprised 92 to 96% of the total. The contribution of power generation was never above 0.4%, while sugar processing accounted for 4 to 8% of the estimated emissions.

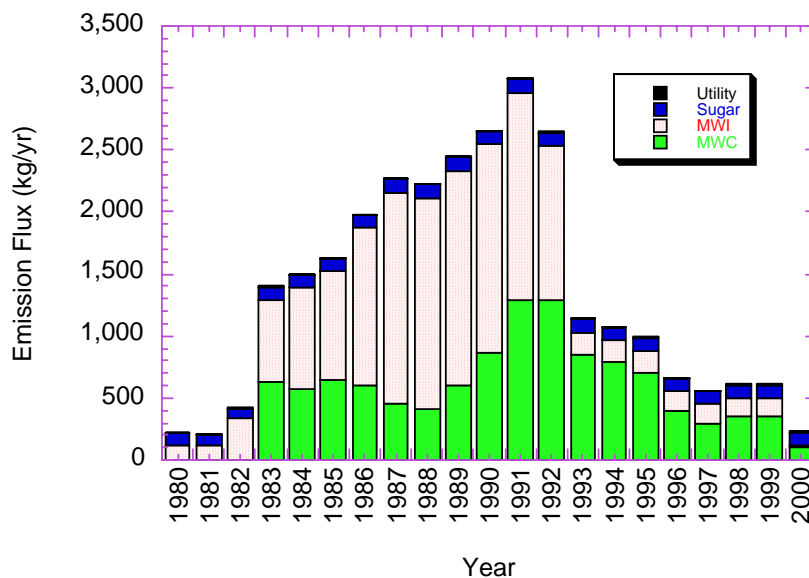


Figure 1. Annual atmospheric mercury emissions in south Florida, 1980 – 2000, estimated by RMB (2002) as a function of major combustion source category. Sources include power generation facilities (Utility), municipal waste combustors (MWC), medical waste incinerators (MWI), and sugar refineries (Sugar). Note: Utility emissions are too small to be discernable in this graphic.

As more stringent regulatory requirements took effect in 1994, many MWI’s ceased operations and medical waste was sent offsite for autoclaving and landfilling rather than incinerated. As a result, local emissions declined sharply through 1993 (65% compared to 1991 levels), followed by a slower and nearly monotonic rate of decline through 2000. The total estimated decline in local emissions between 1991 and 2000 is 2,846 kg/yr, which equates to a total reduction of nearly 93%.

Figure 2 shows the results from the materials flows analysis conducted by Husar and Husar (2002) for Broward, Dade, and Palm Beach counties. Use categories that contributed most greatly to the flow of mercury through south Florida included electrical (e.g., batteries, lighting, and switches), laboratory use, and control (measuring and control instruments) categories. Although coal is the largest source (45%; 65 Mg/yr) of mercury emissions for the US (total 144 Mg/yr), little coal combustion occurs in south Florida and only oil and product-related emissions occur.

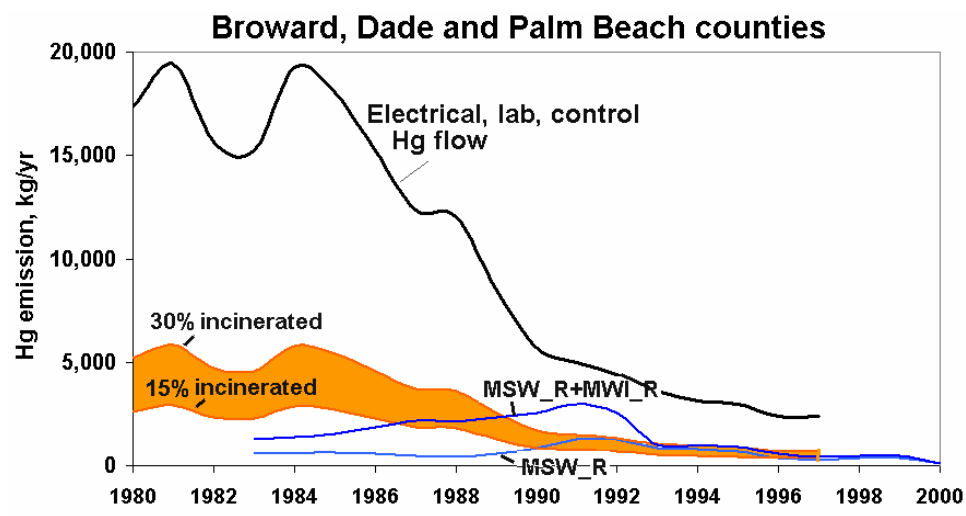


Figure 2. Waste incineration emissions for Dade, Broward, and Palm Beach counties, Florida, inferred from analysis of mercury usage, 1980 to 1997. Upper line shows annual total mercury usage based on different usages. Emission fluxes are based on 30% and 15% incineration rates (complete mobilization of combusted fraction). Plot also shows emissions for MSW and combined MSW and MWI sources estimated by RMB (2002). From Pollman et al. (2002).

1.2 Trends in Mercury Deposition

An essentially continuous record of wet deposition fluxes and concentrations of mercury are available from November 1993 through December 2002 for samples collected from the Beard Research Center in Everglades National Park as part of the Florida Atmospheric Mercury Study (FAMS, 1993-1996, Pollman et al., 1995) and the Mercury Deposition Network (MDN; MDN, 1996-2002; <http://nadp.sws.uiuc.edu/mdn>). The FAMS data consist of integrated monthly wet deposition measurements (Guentzel et al., 2002)), while the MDN data consist of integrated weekly samples. During 1996, monitoring from both studies overlapped for the entire year, and comparison of monthly results demonstrated excellent agreement between the two programs (Pollman and Porcella, 2002). As a result, we combined the two studies to form a period of record of eight full years.

Smoothed time series were constructed for mercury deposition, rainfall depth, and volume weighted mean (VWM) mercury concentrations in wet deposition using 12-month running averages derived from the integrated FAMS-MDN data set. As illustrated in Figure 3, rainfall depth and deposition flux are very closely related¹ and it is difficult to

¹ This is, of course, because deposition fluxes are the product of weekly volume-weighted mean concentration and rainfall depth.

discern without further analysis whether any declines in wet deposition fluxes have occurred unrelated to changes in precipitation. Changes in VWM mercury concentrations are a less ambiguous indicator of whether changes in the atmospheric mercury signal have occurred, although precipitation depth does exert some influence on wet deposition concentrations through washout, particularly when the sample integration period is short. Plotting the running average annual VWM as a function of time indicates that VWM mercury concentrations have declined by 25% since late 1993 (Figure 4).

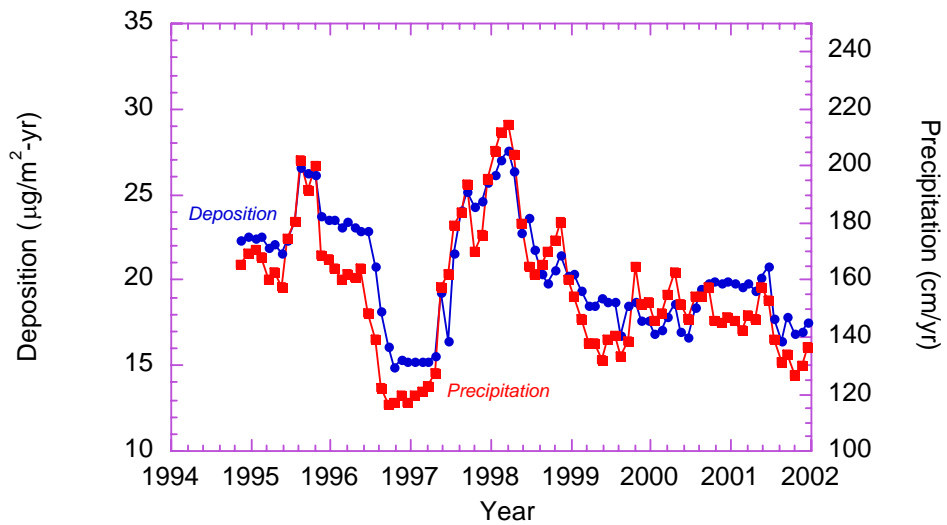


Figure 3. Annual precipitation depth and wet deposition fluxes of mercury measured at Beard Research Station in Everglades National Park, 1993-2002. Data are plotted on a monthly basis as the 12-month running total flux or depth. Data are from the FAMS study (Guentzel et al., 2002) and the MDN network. Squares represent precipitation; circles represent deposition.

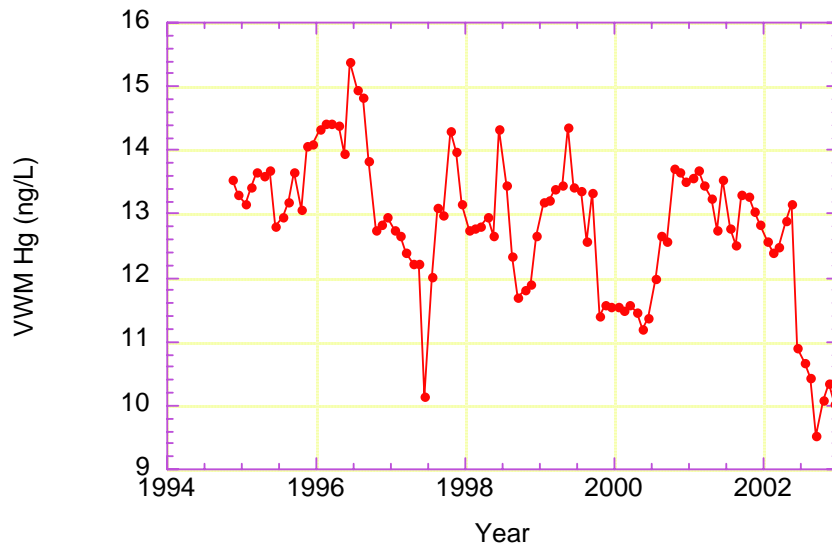


Figure 4. Annual volume weighted mean (VWM) mercury concentration in wet deposition at Beard Research Station, Everglades National Park. Plotted on a monthly basis is the 12-month running average VWM concentration. Data are from the FAMS study (Guentzel et al., 2002) and the MDN network.

An alternative analytical approach using analysis of variance (ANOVA; SAS, 1995) was used to eliminate possible confounding effects of both rainfall depth and seasonal dynamics on wet deposition concentrations. Guentzel et al. (2002) demonstrated that very strong seasonal dynamics consistently underlie wet deposition mercury concentrations in Florida within any given year; as a result, a seasonal dummy variable (D_{month}) based on a sinusoidal transformation on the month of year the sample was collected was created and input to the model. The dummy variable had the following form:

$$D_{month} = A \cdot \sin\left(\frac{M^* \cdot \pi}{12}\right) + B$$

where A and B are fitted using non linear least squares regression (SAS, 1995) and are equal to 8.8827 and 6.6954, respectively, and M^* is the number of the month (*viz.*, 1 through 12), adjusted using a one month offset so that predicted and observed peak values occurred during the same month. Residuals from the ANOVA model for VWM

mercury plotted as a function of time are shown in Figure 5 and demonstrate that a statistically significant decline ($p = 0.0413$) in VWM mercury concentrations occurred over the period of record. Between 1994 and 2002, the analysis indicates that VWM mercury concentrations declined by approximately 3 ng/L due to factors other than seasonal dynamics and rainfall depth.

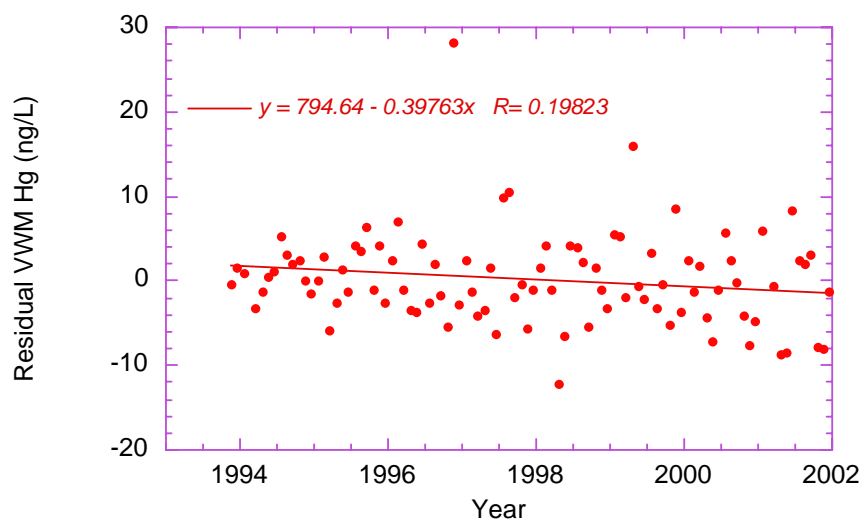


Figure 5. Plot of monthly residuals of ANOVA model of mercury deposition as a function of time. Slope of regression line is significant at $p = 0.0413$.

The declines in measured VWM concentrations are considerably smaller than the overall decline in local emissions estimated to have occurred since the late 1980's and early 1990's (Figure 1 and Figure 2). However, most of the decline in emissions occurred prior to late 1993 when monitoring of mercury concentrations in wet deposition first began. Indeed, the relatively modest change in VWM concentrations agrees reasonably well with the emissions declines after 1993 (Figure 6).

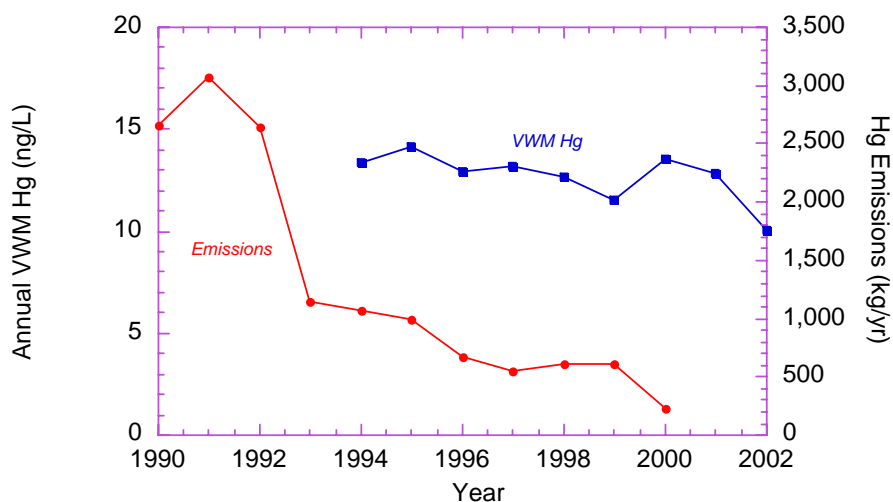


Figure 6. Annual VWM concentrations of mercury measured in wet deposition at Beard Research Center, Everglades National Park, and estimated mercury emissions from Dade, Broward, and Palm Beach counties. Emissions estimates from RMB (2002).

1.3 Trends of Mercury in Everglades Biota

Two data sets are available to examine recent trends in mercury concentrations in biota in the Everglades: (1) the data of Lange et al. (2003), who have collected and analyzed largemouth bass for tissue concentrations of mercury from sites throughout Florida since 1988; and (2) the data of Frederick et al. (2001), who examined mercury concentrations in the feathers of great egret chicks, also throughout Florida and including seven sites in south Florida since 1994. Pollman et al. (2002) analyzed the significance of biota temporal trends using the Mann-Kendall Slope Test-of-Sign. This method is a non-parametric test for zero slope that calculates the slope for each possible pairwise combination of observations in the data set, and then ascribes a value of 1, 0, or -1 to the result based on the whether the slope is positive, zero, or negative.

Largemouth bass mercury concentrations for 12 sites across Florida (including 9 sites in the Everglades) were analyzed for trend significance. The period of record analyzed extended from as early as 1988 to as late as 2003. The data were stratified according to age class since different age classes in any given year reflect different exposure histories. Of a possible 120 categories (*i.e.*, 10 age classes x 12 sites), 66 had sufficient data to test

for sign significance (Table 1). The results were split relatively evenly between a significant decline at the 95% confidence level (29 site-cohort combinations) and no trend (34 site-cohort combinations). Significant declines were observed across the state, suggesting a regional effect (e.g., atmospheric deposition), with the most consistent declines across cohorts observed for the two Everglades canal sites, L-67A and L-35B and East Lake Tohopekaliga (Figure 7 and Figure 8, respectively). The three sites in WCA-3A near site 3A-15 (located near the so-called “hot spot” of high fish tissue mercury concentrations in WCA-3A) also showed some cohorts with significant declines, although nearly as many site-cohort combinations also showed no change. Only three site-cohort combinations showed a significant increasing trend, and these all were observed at the U3 site in WCA-2A. This increase likely reflects a highly localized effect both in time and space, such as peat burning and oxidation that occurred in the Everglades following the intense drought and dry-down in May and June 1999 (Pollman et al., 2002). This period of peat oxidation induced a series of short-term but substantial changes in mercury biogeochemistry, including large scale increases in mosquitofish mercury concentrations at site U3, while the response at 3A-15, which remained wet during this period, was more muted (Krabbenhoft and Fink, 2001).

Table 1. Summary of Mann-Kendall Slope Test-of-Sign for trends in mercury concentrations in largemouth bass. Test results are given for individual sites and age cohorts. (-) indicates significant declining trend; (0) indicates no significant trend; and (+) indicates significant increasing trend. Site-cohort combinations with insufficient data are left blank. All results reported at the 95% significance level.

Location\Age Class	0	1	2	3	4	5	6	7	8	9
Northern Florida										
Fowlers Bluff		0	0	-	0	0	-	0	0	
Central Florida										
Lake Tohopekaliga		0	-	0	-	0	0			0
East Lake Tohopekaliga		-	-	-	-	-	-	0		
Everglades										
Miami Canal and L-67A		-	-	-	-	-	0	-		
L-35B Canal		0	-	-	-	-	0			
Indian Camp Creek-Rogers		0	0		0	0				
Marsh-15	-	-	0	0	0					
Marsh-GH	0	-	0	-						
Marsh-OM		-	-							
Marsh-U3	+	+	+	0	0					
Big Lostmans Creek	0	0	0	0	0					
North Prong	0	-	0	-	-	0				

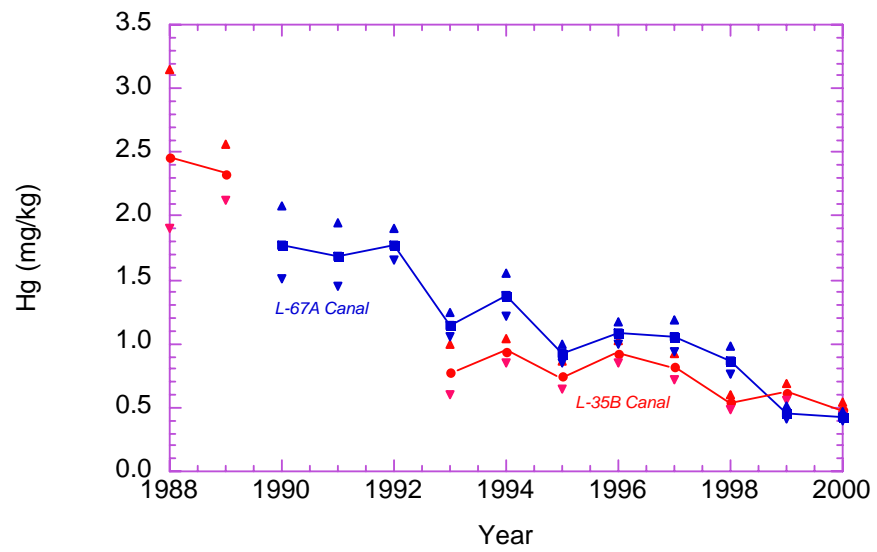


Figure 7. Tissue concentrations of mercury (wet weight) in largemouth bass from the L-67A and L-35B canals in the Florida Everglades. Filled circles and squares show the geometric mean for a respective site each year; filled triangles show \pm one standard error of the mean.

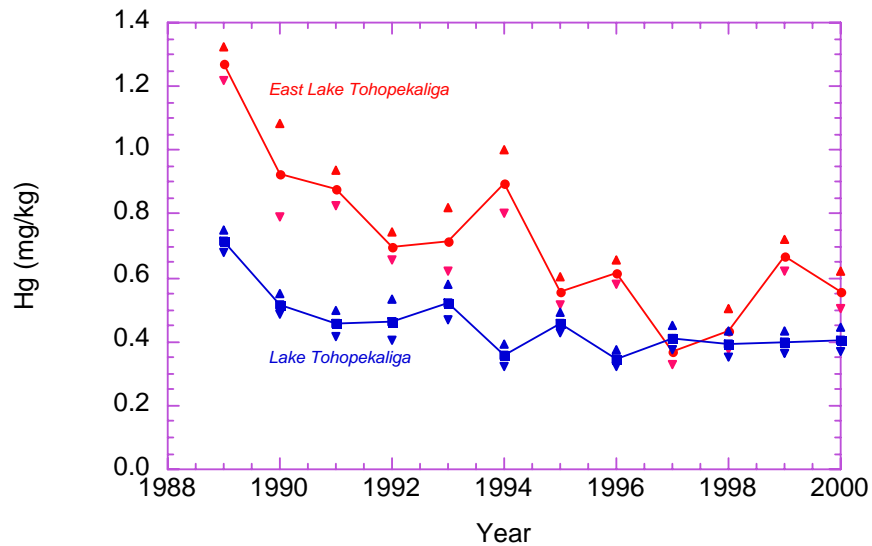


Figure 8. Tissue concentrations of mercury (wet weight) in largemouth bass in East Lake Tohopekaliga and Lake Tohopekaliga located in central Florida. Points show the geometric mean for each year; filled triangles show \pm one standard error of the mean.

Great egret chick feather data from all seven sites studied by Frederick et al. (2001) also were tested for trend significance. When Pollman et al. (2002) conducted their trend significance analysis, the time frame spanned by the great egret study extended from 1994 to 2001. Additional data have since been collected, and the full period of record now extends to 2003 (Figure 9). Four sites (Alley, Hidden, JW1, and L67) showed significant downward trends through 2001 based on both the Mann-Kendall test and Sen's median slope analysis. The data from 2002 and 2003 further substantiate the overall robustness of the downward trend. Consistent with the largemouth bass results from the same region, results from great egret colonies located in the mid-Everglades indicate over an 80% decrease in mercury concentrations over the period of 1994-2003.

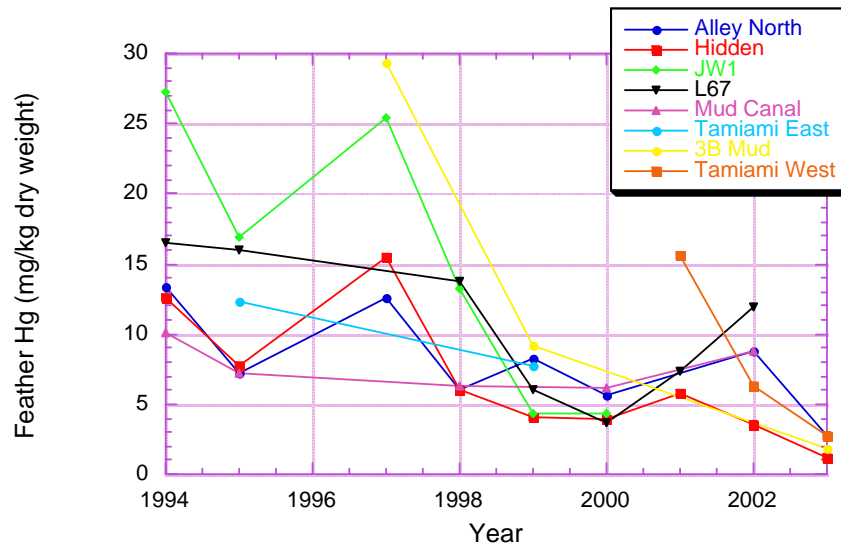


Figure 9. Mercury concentrations in great egret nestlings at various colony locations in the Florida Everglades, 1994 – 2003. Discontinuities in the period of record reflect years when a colony site was abandoned or otherwise not used. Unpublished data courtesy of P. Frederick (2003).

1.4 Model Hindcasting

The Everglades Mercury Cycling Model (E-MCM) was used to predict changes in age 3 largemouth bass mercury concentrations in response to assumed changes in atmospheric loadings of mercury to site 3A-15, a site which has long been considered a mercury ‘hot spot’ in the central Everglades, and which has also experienced recent declines in LMB mercury concentrations. Originally adapted to the Everglades using the Mercury Cycling Model (MCM; Hudson et al., 1994) as the model framework, E-MCM in its present incarnation has been calibrated and applied to at least six Everglades sites (Harris et al., 2003), including site 3A-15. A simplified trajectory of changing deposition rates from 1900 through 2000 was developed with several assumptions or constraints imposed:

1. Based on mercury accumulation rates measured in soil cores in WCA-2A (Rood et al., 1995), an increase in modern deposition rates of 8.7-fold (1985 to 1991) over “pre-industrial” (ca. 1900) was assumed. Rood et al.

measured an average accumulation rate of $8 \mu\text{g}/\text{m}^2\cdot\text{yr}^{-1}$ for ca. 1900, which yields a modern peak deposition flux of $69.6 \mu\text{g}/\text{m}^2\cdot\text{yr}^{-1}$ for 1985-1991.

2. We assume that, superimposed upon the long-term background deposition of $8 \mu\text{g}/\text{m}^2\cdot\text{yr}$ inferred from Rood et al., there has been a deposition signal derived from anthropogenic sources (local and larger geographic scale) that tracks the 1970-2000 mercury trend in the municipal solid waste (MSW) inventory compiled by Kearney and Franklin Associates (1991). This inventory shows that mercury in MSW peaked between 1985 and 1990, with a comparatively sharp decline through 1995, followed by relatively stable inventory quantities. As a first order analysis, we also assumed that anthropogenic emissions and associated deposition fluxes increased linearly from 1900 through 1991, with 1991 corresponding to the year of peak local emissions.

3. After emissions and deposition reached peak levels in 1991, we assumed that deposition declined linearly until 1996, with total mercury deposition reduced to $35 \mu\text{g}/\text{m}^2\cdot\text{yr}^{-1}$. Following 1996, we assume deposition fluxes declined another 25% consistent with declines in VWM concentrations in wet deposition observed in south Florida (Figure 4). Figure 10 shows the mercury deposition trajectory that resulted from these assumptions.

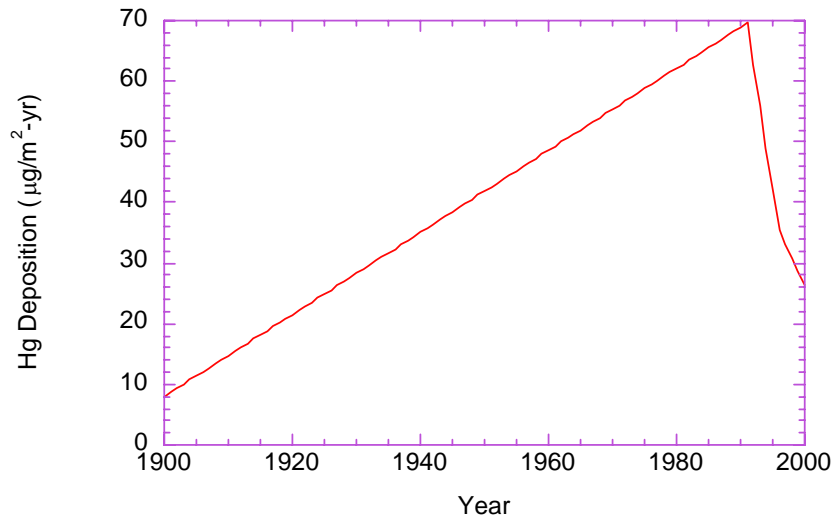


Figure 10. Total (wet + dry deposition) mercury deposition trajectory used in E-MCM model hindcast.

The mercury deposition trajectory was then used as the input forcing function to reconstruct a predicted time series of biotic (largemouth bass) response in south Florida using the E-MCM model. E-MCM was initially run at pre-1900 deposition conditions until steady-state was achieved in all the model compartments (water, sediments, and biota). The model then was perturbed by imposing the reconstructed deposition time series, and the predicted biota response compared to the observed trends for ca. 1990-2000.

Testing of the response time of the E-MCM model to perturbations in mercury loadings has shown that the recovery period predicted by the model is sensitive to the size of the pool of Hg(II) in the sediments available for methylation. Mesocosm experiments currently underway in the Everglades indicate that mercury methylation rates and transfer to the aquatic food chain respond very rapidly in response to new inputs of Hg(II) (D. Krabbenhoft, pers. comm.). These experiments are being conducted using isotopic tracers to elucidate the magnitude and timing of changes in mercury cycling to changes in mercury inputs. Similar results are emerging

from the *Mercury Experiment To Assess Atmospheric Loading in Canada and the United States* (METAALICUS; R. Harris, pers. comm.), which also employs isotopic tracers. E-MCM predicts that the primary pathway for introducing mercury into the food chain at site 3A-15 is via methylation in the sediments and through the benthic food web. Thus, the magnitude of the predicted response is governed by the residence time of bioavailable mercury in the sediments, which in turn is governed at least in part by the mixed depth of actively exchanging surficial sediments. In light of the recent isotopic tracer experimental results, the traditionally assumed exchange depth of 3 cm often employed in the model is likely to prove to be a large overestimate of the size and residence time of the Hg(II) pool available for methylation. As a result we conducted the hindcast simulation assuming a sediment exchange depth of 1 cm.

The resultant hindcast indicates that the assumed declines in atmospheric inputs can explain nearly 60% of the observed decline in observed trends in largemouth mercury concentrations (a predicted 48% decline vs. an observed 75% decline; Figure 11). Likewise, the predicted timing of the biota decline is concordant with the observed results. The fraction of the observed decline unexplained by the model hindcast may reflect several factors. First, the reconstructed deposition trajectory may reflect an underestimation of the effects local sources historically exerted on mercury deposition rates in the Everglades. For example, the simulation assumes that the decline in deposition between 1991 and 2000 was 62%, compared to a biota decline approximating 75%. Given the essential linearity of the longterm response of the model (Harris et al., 2001), the hindcast at most would predict a 62% decline. Second, we likely have underestimated the rapidity of the sediment response by assuming an exchange depth of 1cm rather a shallower depth interval. Reducing the exchange depth would bring the slope of the predicted response closer to the slope of the deposition trajectory, which in turn is nearly coincident with the slope of the observed biotic response. Third, the larger observed response may also reflect changes in other environmental variables during the same period – in particular declining surface water sulfate concentrations observed at the site which can influence rates of methyl mercury production (Pollman et al., 2004). The effects of these other variables need to be examined more carefully before more definitive conclusions on causality can be reached.

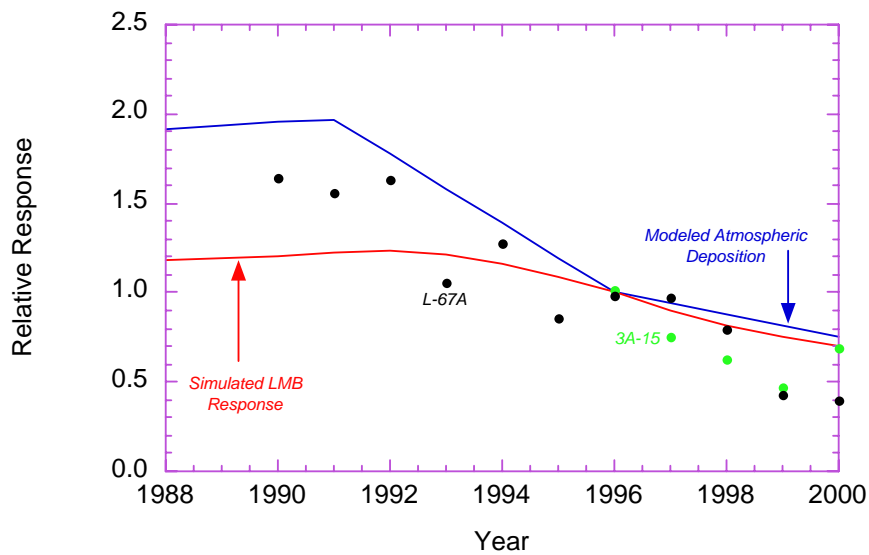


Figure 11. E-MCM simulation hindcast of changes in mercury concentrations in largemouth bass age 1 cohorts at 3A-15 in response to assumed changes in atmospheric deposition. Analysis assumes that the depth of surficial sediments actively exchanging Hg(II) is 1 cm. Shown are normalized (relative to 1996) changes in atmospheric deposition inputs, observed concentrations in largemouth bass (filled circles) for both 3A-15 and the L-67A canal located approximately 20 km east of 3A-15.

Discussion and Conclusions

Local atmospheric emission rates of mercury in south Florida appear to have declined by over 90% since peak levels occurring in the late 1980's to early 1990's. This estimate is supported by two independent approaches to estimating emissions. Whether these changes in emissions have had a corresponding effect on local deposition rates of mercury is in part a function of the chemical speciation of the emissions. There are two major types of gas phase mercury species present in emissions from combustion sources: elemental mercury or Hg(0), and reactive gaseous mercury (RGM) or Hg(II). Speciation of emissions is critical because it influences greatly how far emitted mercury likely will be transported. Hg(0) reacts in and is deposited from the atmosphere only very slowly, and has a characteristic

residence time in the troposphere on the order of 6 months. RGM, on the other hand, is highly reactive and is scavenged rapidly from the lower troposphere by either wet deposition or by dry deposition processes.

If, for example, there had been a decline in Hg(0) emissions from south Florida, but RGM emissions remained constant, we would expect little or no change in biota mercury concentrations in the Everglades as a result. On the other hand, if local RGM emissions had declined, but Hg(0) emissions remained constant, one would expect to see more of a biotic response. By not considering speciation, we risk misinterpreting the true significance of the relationship between local emissions and biotic response. This would be particularly true if Hg(0) emissions greatly predominate. Unfortunately only limited data are available on the speciation of mercury emissions as a function of source, including speciation measurements conducted by Dvonch et al. (1999) from a municipal waste incinerator (8 measurements), a medical waste incinerator (3 measurements) and a cement kiln (3 measurements) in Dade and Broward counties. The fraction of RGM emitted ranged from 25% of the total (cement kiln) to nearly 95% for the medical waste incinerator. The fraction of RGM emitted by the municipal waste incinerator averaged ca. 75%. Since the local emissions inventory for Dade and Broward counties in 1995-96 was dominated by municipal waste and medical waste incineration (ca. 86% of total emissions), it appears likely that RGM emissions were predominant, at least for 1995-96. If these speciation results are similar for historical emission patterns (and there is no reason to expect that Hg(0) emissions were more important), then our approach of examining total emissions and linking the trends to local biota response appears reasonable.

Coupled with changes in local emission rates is evidence that mercury concentrations in wet deposition (annual VWM) in south Florida have declined by about 25% since late 1993. Statistical analysis indicates that the trends are significant, and are due to factors other than seasonal dynamics and changes in precipitation rates. Although the declines in measured VWM concentrations are considerably smaller than the overall decline in local emissions, most of the decline in emissions occurred prior to late 1993 when monitoring of mercury concentrations in wet deposition first began. Indeed, the relatively modest change in VWM concentrations agrees reasonably well with the emissions declines after 1993.

Statistically significant declines in mercury concentrations in both largemouth bass and great egret chicks have been observed for a number of

sites in the Everglades. Declines for both species are on the order of 75 to 80% over approximately the past decade. Model hindcasting using the E-MCM model calibrated for site 3A-15 indicates that changes in atmospheric deposition inferred from sediment core analyses may account for most if not all of the recent changes in largemouth bass mercury concentrations, both in terms of timing and magnitude of change, although the effects of concomitant shifts in other environmental variables (*viz.*, surface water sulfate concentrations) need to be elucidated further. These results are predicated on rapid rates of turnover of the pool of Hg(II) that is readily bioavailable in surficial sediments for methylation, and are consistent with recent isotopic tracer experiments indicating that mercury cycling in aquatic systems responds very rapidly to recent inputs.

Further research, analyses and modeling will explore the uncertainties in the model with the aim of better constraining the processes that govern interactions at the sediment-water interface and the timing of this interaction. Additional improvements will be pursued to refine the E-MCM to improve it as a tool to support environmental policies such as total maximum daily load analyses throughout Florida.

1.5 References

- Atkeson, T.D. and C.D. Pollman. 2002. *Trends of mercury in Florida's environment: 1989-2001*. Presented at the 23rd ACS National Meeting, April 7-11; Orlando, FL
- Dvonch, J.T., J.R. Graney, G.J. Keeler and R.K. Stevens. 1999. *Utilization of elemental tracers to source apportion mercury in South Florida Precipitation*. *Env Sci Technol.*: 33: 4522-4527
- Pollman, C., G. Gill, W. Landing, J. Guentzel, D. Bare, D. Porcella, E. Zillioux, and T. Atkeson. 1995. *Overview of the Florida Atmospheric Mercury Study*. *Water, Air & Soil Poll.*, 80:285-290
- Frederick, P. C., M. G. Spalding and R. Dusek. 2001. *Wading birds as bioindicators of mercury contamination in Florida: annual and geographic variation*. *Env Toxicol Chem*: 21:262-264
- Guentzel, J.L., W.M. Landing, G.A. Gill, and C.D. Pollman. 2001. *Processes Influencing Rainfall Deposition of Mercury in Florida*. *Env. Sci. Technol.*: 35: 863-873.
- Harris, R., C. Pollman, D. Hutchinson and D. Beals. 2001. Florida Pilot Mercury . Total Maximum Daily Load (TMDL) Study: Application of the Everglades Mercury Cycling Model (E-MCM) to Site WCA 3A-15.

- Report submitted to Florida Department of Environmental Protection. Tetra Tech, Inc., Lafayette, CA.
- Harris, R., D. Beals, D. Hutchinson and C. Pollman. 2003. Mercury Cycling and Bioaccumulation in Everglades Marshes: Phase III Report. Final Draft. Report submitted to Florida Department of Environmental Protection. Tetra Tech, Inc., Lafayette, CA.
- Hudson, R.J.M., S.A. Gherini, C.J. Watras, and D.B. Porcella. 1994. Modeling the biogeochemical cycle of mercury in lakes: The Mercury Cycling Model (MCM) and its application to the MTL study lakes. In C.J. Watras and J. W. Huckabee [eds.], Mercury Pollution – Integration and Synthesis. CRC Press Inc. Lewis Publishers.
- Husar, J.D. and R.B. Husar. 2002. *Trends of anthropogenic mercury mass flows and emissions in Florida*. Final Report, Lantern Corporation, Clayton, MO. 74 pp, Typescript
- Kearney and Franklin, Assoc. 1991. Characterization of Products Containing Mercury in Municipal Solid Waste in the United States, 1970-2000 by A. T. Kearney, Inc. and Franklin Associates, Inc. to US EPA, 4/92 NTIS# PB92-162 569.
- Krabbenhoft, D.P. and L.E. Fink. 2001. *The effect of dry down and natural fires on mercury methylation in the Florida Everglades*. Appendix 7-8 in Everglades Consolidated Report, South Florida Water Management District, West Palm Beach, FL
<http://www.sfwmd.gov/org/ema/everglades/previous.html>
- Lange, T., D. Richard, B. Sargent and E. Lundy. 2003. Fish Tissue Monitoring Report. Florida Fish and Wildlife Conservation Commission, Environmental Research Institute, Eustis, Florida. 14pp.
- NADP, 2002. National Atmospheric Deposition Program, Mercury Deposition Network. National Atmospheric Deposition Program (NRSP-3)/Mercury Deposition Network. (2002). NADP Program Office, Illinois State Water Survey, 2204 Griffith Drive, Champaign, IL 61820).
<http://nadp.sws.uiuc.edu/mdn/>
- Pollman, C.D., G.A. Gill, W.M. Landing, J.L. Guentzel, D.A. Bare, D. Porcella, E. Zillioux, and T. Atkeson. 1995. Overview of the Florida Atmospheric Mercury Study (FAMS). *Water, Air, and Soil Pollution* 80: 285-290.
- Pollman, C.D. and D.B. Porcella. 2002. Assessment of trends in mercury-related data sets. Air Waste Management Association, Florida Section, Annual Meeting. 15-17 September 2002, Jupiter Beach, FL.
- Pollman, C.D. and D.B. Porcella. 2002. Trends in mercury emissions and concentrations in biota in south Florida: A critical Analysis. Final Report to the Florida Electric Power Coordinating Group. 19 June, 2002. 46 pp, Typescript.

- Pollman, C.D. and D.B. Porcella. 2003. Assessment of trends in mercury-related data sets. *J. Phys. IV France* 107: 1083-1090.
- Pollman, C.D., R. Harris, D.B. Porcella, and D. Hutchinson. 2004. Have Changes in Atmospheric Deposition Caused Concomitant Changes in Largemouth Bass Concentrations in the Florida Everglades – A Model Hindcast Analysis. 7th International Conference on Mercury as a Global Pollutant, 27 June – 2 July, 2004, Ljubljana, Slovenia.
- RMB Consulting & Research, Inc. 2002. Atmospheric mercury emissions from major point sources – Broward, Dade, and Palm Beach Counties, 1980-2000. Draft Final Report, RMB Consulting & Research, Inc., Raleigh, NC
- Rood, B.E., J.F. Gottgens, J.J. Delfino, C.D. Earle, and T.L. Crisman. 1995. *Mercury accumulation trends in Florida Everglades and Savannas Marsh flooded soils*. *Water, Air & Soil Poll.*; 80:981-990
- Stober, Q.J., K. Thornton, R. Jones, J. Richards, C. Ivey, R. Welch, M. Madden, J. Trexler, E. Gaiser, D. Scheidt, and S. Rathbun. 2001. *South Florida Ecosystem Assessment: Phase I/II – Everglades Stressor Interactions: Hydropatterns, Eutrophication, Habitat Alteration, and Mercury Contamination* (Summary). EPA 904-R-01-002. USEPA Region 4 Science & Ecosystem Support Division, Water Management Division, and Office of Research and Development