ATMOSPHERIC DEPOSITION of NITROGEN and AIR TOXINS to the TAMPA BAY ESTUARY

FINAL REPORT

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Atmospheric Deposition of Nitrogen and Air Toxins to the Tampa Bay Estuary

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# Table of Contents

Acknowledgements .............................................................................................................................. 2
Table of Contents .................................................................................................................................. 3
List of Figures .......................................................................................................................................... 4
List of Tables .......................................................................................................................................... 6
Atmospheric Deposition of Nitrogen and Air Toxins to the Tampa Bay Estuary Final Report .......................................................... 7

1. INTRODUCTION ............................................................................................................................. 7
   1.1 History of TBADS ......................................................................................................................... 8
   1.2 From TBADS to BRACE ............................................................................................................. 10
   1.3 Role of Nitrogen .......................................................................................................................... 10
   1.4 Role of Air Toxins ....................................................................................................................... 11

2. NITROGEN ......................................................................................................................................... 13
   2.1 Wet and Dry Deposition Rates ................................................................................................. 13
   2.2 Coarse Particle Nitrogen ........................................................................................................... 16
   2.3 Organic Nitrogen ......................................................................................................................... 18
   2.4 Spatial Gradient of Ammonia Across Urban Tampa ..................................................................... 20
   2.5 Bi-Directional Ammonia Flux at the Air/Water Interface .......................................................... 25
   2.6 Sources of Ambient Air Nitrogen ............................................................................................... 25
   2.7 Summary .................................................................................................................................... 33
   2.8 Recommendations ...................................................................................................................... 33

3. AIR TOXINS ..................................................................................................................................... 35
   3.1 Polychlorinated Biphenyls (PCBs) ............................................................................................ 35
   3.2 Organochlorine Pesticides ......................................................................................................... 36
   3.3 Polycyclic Aromatic Hydrocarbons (PAHs) ............................................................................... 43
   3.4 Metals ....................................................................................................................................... 52
   3.5 Summary and Recommendations ............................................................................................... 62

4. REFERENCES ..................................................................................................................................... 64

APPENDIX A METHODS ....................................................................................................................... 74
   Nitrogen ........................................................................................................................................... 74
   Metals ............................................................................................................................................... 76
   PCBs, PAHs and Organochlorine Pesticides .................................................................................... 78

APPENDIX B TBADS AND BRACE PUBLICATIONS .......................................................................... 83

APPENDIX C BRACE OBJECTIVES AND MEASUREMENTS MATRIX .................................................... 91
List of Figures

Figure 1. Monthly dry deposition of nitrogen to Tampa Bay, August 1996-July 2001.................................................14
Figure 2. Monthly wet deposition of nitrogen to Tampa Bay, August 1996-July 2001......................................................14
Figure 3. Monthly total deposition of nitrogen to Tampa Bay, August 1996-July 2001......................................................15
Figure 4. Average daily concentrations of ambient air ammonia as a function of wind speed, and direction. Ammonia concentrations were measured with an annular denuder system over a three-year period on a 1-in-6 day schedule; average daily resultant wind speed and direction at Tampa International Airport were obtained from the National Climatic Data Center website (NCDC, 2001). Jimmy Foster, June 2001, prepared the graph.................................................................16
Figure 5. Size distributions for sodium, chloride and nitrate collected at the eastern end of the Gandy Bridge from October to November 2001. Backwards air mass trajectories computed with the NOAA HYSPLIT model (NOAA, 2001) showed (a) marine, (b) mixed marine and terrestrial, and (c) terrestrial wind origins.......................17
Figure 6. Atmospheric deposition rates of organic amine nitrogen and ammonium nitrogen in bulk deposition samples collected at a bayside site in Tampa, Florida. These rates include days with and without rainfall (Hendrix, et al., 2002)...18
Figure 7. Daily dry ammonia/ammonium fluxes estimated from bulk deposition measurements and from inferential modeling based on ambient air concentrations obtained from the annular denuder system (ADS), October 2001 to November 2001. ..................................................................................................................................................20
Figure 8. Two-week averaged ammonia concentration gradient across urban Tampa, October 2001 (Tate, 2002). The numbers indicate inventoried ammonia emission sources, as described in Table 2. Units for the color scale are µg/m³........................................................23
Figure 9. USGS aerial photograph of Hooker’s Point, Tampa, showing the deep-water ports and industrial complexes. In the months prior to deployment of the PSD network, preliminary or “scoping” ammonia concentration measurements were made by PSD at 4 sites on Hooker’s Point: (S) adjacent to Howard Curran wastewater treatment plant sludge drying beds; (R) next to the railway conveyance for product transfer; (F, D) close to the docks.............................................................................................................................24
Figure 10. Plot of ammonium nitrogen in Tampa Bay for January 2002. Graphic is courtesy of the Environmental Protection Commission of Hillsborough County..........................................................26
Figure 11. Ammonia emissions by source category for Pinellas and Hillsborough County. The inventory was assembled by Connie Mizak, June 2001, with data from CMU (2001), the TRI (2001) and the USEPA (2001); and updated by Scott Mower, February, 2002. ..................................................................................................................27
Figure 12. Average daily concentrations of ambient air nitric acid as a function of wind speed and direction. Nitric acid concentrations were measured with an annular denuder system over a three-year period on a 1-in-6 day schedule; average daily resultant wind speed and direction at Tampa International Airport were obtained from the National Climatic Data Center website (NCDC, 2001). Jimmy Foster, June 2001, prepared the graph.................................................................28
Figure 13. Rainwater concentrations (top) and nitrogen wet deposition rates (bottom) by air mass trajectory for nitrate and ammonia (Smith, et al., 2001). Analyzed were 293 daily rainfall samples collected at the Gandy Bridge site from August 1996 to December 2001. Trajectories were obtained from the NOAA HYSPLIT website (http://gus.arl.noaa.gov/ready/hysplit4.html)...............................................................................................................32
Figure 14. Daily pesticide concentrations observed on a 1-in-6 day sampling schedule from March-October 2001 at the Gandy Bridge site in Tampa, Florida.................................................................................................38
Figure 15. A comparison of the 1995 (Frithsen et al., 1995) and 2001 direct atmospheric loading of pesticides to the Tampa Bay Estuary........................................................................................................39
Figure 16. Correlation of endosulfan (r=0.15) and chlordane (r=0.58) with average daily wind speed. Wind speed was obtained for the Tampa International Airport from the National Climatic Data Center website. Chlordane and endosulfan concentrations were measured at the Gandy Bridge site in Tampa, Florida, from March-October, 2001. For chlordane, an exponential model fit the data better than a linear model, but neither model fit the endosulfan data........................................................................................................................................41
Figure 17. Clausius-Clapeyron plots for endosulfan (r=-0.02) and chlordane (r=-0.59). Average daily temperatures were obtained for the Tampa International Airport from the National Climatic Data Center website. Chlordane and endosulfan concentrations were measured at the Gandy Bridge site in Tampa, Florida, from March-October, 2001. ........................................................................................................................................42
Figure 18. Ratio of γ- to α-chlordane. Lower ratios imply more photodegradation of the γ isomer, and thus a longer transport distance..................................................................................................................................42
Figure 19. Total daily rainfall was obtained for the Tampa International Airport from the National Climatic Data
Center website. Pesticide concentrations were measured at the Gandy Bridge site in Tampa, Florida, from March-October, 2001............................................................................................................ 43

Figure 20. Daily total PAH concentrations observed on a 1-in-6 day sampling schedule from March-October, 2001 at the Gandy Bridge site in Tampa, Florida............................................................................................................................................. 45

Figure 21. Daily PAH concentrations observed on a 1-in-6 day sampling schedule from March-October 2001 at the Gandy Bridge site in Tampa, Florida......................................................................................................................... 46

Figure 22. Dependence of ambient air fluoranthene ($r = 0.53$), fluorene ($r = 0.27$), pyrene ($r = 0.52$) and phenanthrene ($r = 0.40$) concentrations on average daily wind speed. ........................................................................................................... 49

Figure 23. Dependence of ambient air fluoranthene ($r = 0.33$), fluorene ($r = 0.51$), pyrene ($r = 0.23$) and phenanthrene ($r = 0.49$) concentrations on average daily PM$_{2.5}$ (PMFine) concentration. ................................................................. 49

Figure 24. Clausius-Clapeyron plots for fluoranthene and pyrene. Average daily temperatures were obtained for the Tampa International Airport from the National Climatic Data Center website. Fluoranthene and pyrene concentrations were measured at the Gandy Bridge site in Tampa, Florida, from March-October 2001. ................................................................. 49

Figure 25. Total daily rainfall was obtained for the Tampa International Airport from the National Climatic Data Center website. Ambient air phenanthrene concentrations were measured at the Gandy Bridge site in Tampa, Florida, from March to October 2001............................................................................................ 50

Figure 26. Ambient air phenanthrene ($r = 0.24$) and fluorene ($r = 0.4$) versus nitrogen dioxide (NO$_2$) concentration for measurements made at the Gandy Bridge site in Tampa, Florida, from March to October 2001................. 51

Figure 27. A comparison of the 1995 (Frithsen et al., 1995) and direct atmospheric loading of toxic metals to the Tampa Bay Estuary........................................................... 56

Figure 28. Correlation of aluminum with silicon ($r=0.99$), iron ($r=0.98$), potassium ($r=0.94$) titanium ($r=0.99$), manganese ($r=0.97$), and chromium ($r=0.58$) in ambient air particles 10 µm in diameter or smaller (upper graph); correlation of aluminum with iron ($r=0.97$), manganese ($r=0.96$), titanium ($r=0.82$), and chromium ($r=0.86$) in rainwater (lower graph). ............................................................................................................................... 58

Figure 29. Correlation of copper with zinc ($r=0.75$) and lead ($r=0.65$) in ambient air particles 10 µm in diameter or smaller (upper graph); correlation of copper with zinc ($r=0.80$), lead ($r=0.83$), arsenic ($r=0.79$), and cadmium ($r=0.76$) in rainwater (lower graph). ................................................. 59

Figure 30. Correlation of nickel with vanadium ($r=0.72$) in ambient air particles 10 µm in diameter or smaller (upper graph) and correlation of nickel with vanadium ($r=0.87$) in rainwater (lower graph). ......................................................... 60
List of Tables

Table 1. Annual direct atmospheric nitrogen deposition rates to Tampa Bay for inorganic ammonia/ium plus nitric acid/nitrate. .................................................................................................................. ......................................13
Table 2. Inventoried ammonia emission sources near Hillsborough Bay (TRI, 2001; CMU 2001). .........................22
Table 3. Statistics for precipitation (rain) $\delta^{15}$NH$_4^+$ and $\delta^{15}$NO$_3^-$ and ambient air (dry) total $\delta^{15}$N observations for complete datasets and by wet and dry seasons, reported in % (per mil), n = number of samples in each category. Dry season was defined as October through May and wet season as June through September. Sampling was done at the Gandy Bridge monitoring site in Tampa, Florida. .................................................................................................................................30
Table 4. Statistics for precipitation $\delta^{15}$NH$_4^+$ and $\delta^{15}$NO$_3^-$ and ambient air total $\delta^{15}$N for each trajectory class, reported in % (per mil), n = number of samples in each category. Sampling was done at the Gandy Bridge monitoring site in Tampa, Florida. .................................................................................................................................31
Table 5. Average daily ambient air PCB concentrations measured at the Gandy Bridge monitoring site from March 2001 to October 2001. The detection limit expressed as an ambient air concentration is based on a 324 m$^3$ sampling air volume (n=36). ........................................................................................................................................................................36
Table 6. Average daily ambient air pesticide concentrations measured at the Gandy Bridge monitoring site from March 2001 to October 2001 .................................................................................................................................37
Table 7. Estimated total direct atmospheric loading (kg yr$^{-1}$) of chlordane and endosulfan to the Tampa Bay Estuary. .................................................................................................................................................................39
Table 8. Average daily ambient polycyclic aromatic hydrocarbon (PAH) concentrations measured at the Gandy Bridge monitoring site from March to October, 2001 .................................................................................................................................................................44
Table 9. Comparison of average PAH (gas + aerosol) concentrations measured at the Gandy Bridge site in Tampa, Florida, with PAH concentrations at “background” and urban sites. Concentrations are in ng m$^{-3}$ .................................................................45
Table 10. Estimated total direct atmospheric loading (kg yr$^{-1}$) of PAHs to the Tampa Bay Estuary ............................47
Table 11. Comparisons of net annual gas fluxes for Tampa Bay and Chesapeake Bay monitoring sites (Gustafson and Dickhut, 1997)$^a$ ........................................................................................................................................................................47
Table 12. Correlations between PAHs .................................................................................................................................48
Table 13. Comparison of direct atmospheric deposition rates of metals to Tampa Bay, to the Gulf of Maine (Pike and Moran, 2001), and to Massachusetts Bay (Golomb, et al., 1997). Units are $\mu$g m$^{-2}$ yr$^{-1}$ .................................................................................................................................57
Table 14. Principal components analysis for metals concentrations in rainwater using SAS® PRINCOMP procedure. Positive and negative weights less than 0.25 are shown in a lighter type to de-emphasize their relative importance. ........................................................................................................................................................................61
Table 15. Physical and chemical properties of selected organochlorine pesticides and PAHs .................................93
Atmospheric Deposition of Nitrogen and Air Toxins to the Tampa Bay Estuary Final Report

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1. INTRODUCTION

Urbanization has placed a significant nutrient and pollution burden on Tampa Bay and its adjacent waters (TBNEP, 1996). Nutrients and other pollutants enter the Bay from urban and agricultural runoff, direct industrial and municipal discharges to surface waters, and atmospheric deposition. In recent years concerned resource managers, scientists and citizens have cooperated in an extraordinary way to reduce regional atmospheric emissions of nitrogen and air toxins, and to better understand how atmospheric deposition of air pollutants affects the water quality of Tampa Bay.

This report seeks to synthesize the knowledge gained from the measurement and interpretation of environmental variables as they relate to atmospheric deposition, and to provide the technical basis for development of community control strategies to reduce the loading to Tampa Bay of nitrogen and of persistent, bio-accumulative and toxic compounds.

The first section of this chapter reviews the history of Tampa Bay atmospheric deposition estimates and related research through 2001. This section is an excerpt from Poor and Pribble (2002). The second section describes the history of the Bay Regional Atmospheric Chemistry Experiment (BRACE) and its research agenda for the future. The third and fourth sections of this chapter outline the research objectives for nitrogen and air toxins, respectively, and summarize the earlier atmospheric loading rate estimates. The research objectives provide the framework for the results and discussion presented in this report.

The key research results, their implications and the policy recommendations for the management of atmospheric deposition of nitrogen and air toxins to Tampa Bay are presented in Chapters 2 and 3, respectively. Chapter 4 lists the cited references, and Appendix A gives an overview of the experimental methods and data analysis techniques.

This report has as its basis both published and yet-to-be published research. Appendix B contains the citations, abstracts and availability of published research. In Appendix C is a succinct matrix of the BRACE monitoring and modeling activities. The environmental data and the corresponding data dictionaries are available on compact diskette from the Tampa Bay Estuary Program. Interpretation of the environmental data will evolve along with our knowledge base and from our local, regional, national and even global perspective.

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1.1 History of TBADS

Initial nitrogen and phosphorus loading estimates to Tampa Bay revealed that atmospheric deposition directly to the bay’s surface contributed about 29% of the total nitrogen load and about 31% of the total phosphorus load to the bay (Zarbock et al., 1994). To further assess the contribution of atmospheric deposition to nutrient loading, the TBEP, Hillsborough, Pinellas, and Manatee Counties, and the Florida Department of Environmental Protection (FDEP) asked that the bay be included as an EPA Great Waters Program. The Tampa Bay Atmospheric Deposition Study (TBADS), after approval by the EPA Great Waters Program, began in the spring of 1995, and resulted in dry and wet nutrient deposition data collection from August 1996 through August 2001.

TBADS and NOAA/Great Waters participants agreed on a monitoring site at the eastern end of the Gandy Bridge. Ambient air and rainfall concentration data collected from this site, in concert with meteorological data collected at a mid-bay site, were analyzed to derive the amount of nitrogen and phosphorus being directly deposited to the bay surface. These data were also utilized to estimate contributions of atmospheric deposition to storm water nutrient loadings to the bay.

The Environmental Protection Commission of Hillsborough County (EPCHC) operated and maintained the Gandy Bridge monitoring site and equipment on behalf of the TBEP for the atmospheric deposition studies; Lee Chapin operated and maintained the mid-bay meteorological station and its sensors.

From the first three years of monitoring at the Gandy Bridge monitoring site, the estimates for the direct atmospheric deposition of nitrogen to Tampa Bay were revised downward from 1000 to 760 metric tons/year, or ~24% of the 1985-1991 total nitrogen loads to the bay. For August 1996 through July 1999 the average dry:wet deposition ratio was 0.78, and ammonia gas or rainfall-dissolved ammonium contributed 58% of the total nitrogen deposition (Poor et al., 2001).

Another part of the effort to ascertain the impacts of atmospheric deposition of nutrients to Tampa Bay was an assessment of bulk deposition to the Tampa Bay watershed at seven sites (Dixon et al., 1996). Samples were analyzed for metals, nitrogen, and phosphorus at all sites over a one-year period, with samples from five of the seven sites analyzed for synthetic organics over a 12-week period. Results of the analyses showed that nitrogen loading to the bay from direct atmospheric loadings is 32% of the total nitrogen load to the bay.

This project was followed by an investigation of the relationship between bulk atmospheric deposition and storm water quality, sponsored by the Florida Department of Transportation (Dixon et al., 1998). The goals of this project were to examine spatial variability in bulk deposition and determine any relationships between bulk atmospheric deposition and storm water loadings. Samples were collected at ten sites within the bay’s watershed. Sample analyses showed that ~1.5 times as much nitrogen was found in storm water than was provided by the bulk atmospheric deposition, indicating that sources other than bulk atmospheric nitrogen contributed to the storm water runoff nitrogen load.
Additionally, TBEP funded a study with the goal of estimating the contribution of atmospheric deposition of nitrogen to storm water loading. Utilizing nitrogen concentrations from rainfall events at the Gandy Bridge site and rainfall amounts from the small urban watersheds, a relationship was derived relating nitrogen in storm water to the nitrogen deposited by rainfall events. Results showed that approximately the same amount of nitrogen left the watersheds in storm water runoff as was deposited to the watersheds via rainfall from July-December 1997 (BCI and PBS&J, 1999).

Recommended by the TBADS participants and initiated in 1998 was a study funded by the Florida Department of Environmental Protection (FDEP) on the stable nitrogen isotopes in rainfall and ambient air for the purpose of classifying the natural versus anthropogenic sources of atmospherically depositing nitrogen. Florida A&M University directed the research, with the University of Virginia responsible for the laboratory analyses.

Coincident with the stable isotope study was an 18-month TBEP-funded effort by EPCHC to compare the nitrogen bulk deposition measurements with the estimates derived from separate wet deposition only plus inferential (i.e., modeled) dry deposition rates.

In May 1999, the TBEP funded the University of South Florida (USF) College of Public Health (COPH) to provide technical and administrative assistance with the analysis and interpretation of the atmospheric deposition data derived from the Gandy Bridge monitoring site and the mid-bay meteorological station. As part of this assistance, USF COPH analyzed the stable nitrogen isotope and bulk deposition data along with the nitrogen ambient air and rainwater concentrations (Poor, 2002).

At the same time and with additional funds from the USEPA Region IV, the atmospheric deposition measurements were expanded to include ambient air concentrations of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides, and both ambient air and rainfall concentrations of metals. Sediments of Tampa Bay most heavily impacted by urban or commercial activities have levels of these contaminants that in some cases pose a significant ecological or human health risk (McConnell, et al., 1996). The earliest loading estimates suggested that for some of these toxins the atmospheric loading should not be ignored (Frithsen, et al., 1995). The air toxin measurements began in March 2000 and continued through October 2001.

A consequence of the discovery of the significant ammonia component to the total atmospheric nitrogen deposition, TBADS participants recommended the deployment of passive sampling devices (PSDs) in urban and industrial Tampa to assess the fugitive ammonia emissions from ammonia and ammonium product transport, storage, processing and manufacturing. The earliest attempts to use the PSDs for measuring the relatively low ambient air concentrations met with limited success, but USF COPH continued the testing and by late 2000 with the endorsement of the TBADS participants, the TBEP funded the study. Also funded by the TBEP were further measurements of ambient air coarse particle nitrate, which is formed by the reaction of nitric acid and sea salt, to estimate the coarse particle nitrate contribution to total nitrogen atmospheric deposition.
1.2 From TBADS to BRACE

The Bay Regional Atmospheric Chemistry Experiment (BRACE) research proposes to improve the current nitrogen deposition estimate and source apportionment efforts by expanding the air pollutant monitoring network, by deploying state-of-the-art sensors and monitors, and by analyzing and interpreting meteorological and air pollutant concentration data with the most sophisticated atmospheric chemistry and physics models available. Increased monitoring spatial and temporal resolution is key to understanding the contribution of regional nitrogen emission sources to the total nitrogen deposition. The BRACE is funded by the Florida Department of Environmental Protection (FDEP) and TECO, Inc., trust funds, and by “in-kind” contributions of NOAA, USEPA, and Pinellas County Department of Environmental Management.

The anticipated project length is six years: three years of planning, equipment acquisition, contract negotiations, site identification and preparation, and pilot studies; one month of intensive and one year of baseline monitoring; and three years of receptor modeling and air pollutant transport, dispersion, transformation, and deposition modeling. The purpose of the May 2002 intensive monitoring period was to obtain a sufficient number of high quality observations to initialize and evaluate the air quality models. BRACE research activities began in 1999 and both published (Appendix B) and unpublished results have been incorporated into this report. The BRACE objectives and an overview of the planned measurements are listed in Appendix C.

1.3 Role of Nitrogen

Bricker, et al. (1999) classified Tampa Bay as a highly eutrophic estuary, heavily influenced by anthropogenic activities. Their classification for Tampa Bay was based primarily on the chlorophyll $a$ concentrations, an indicator of algal abundance.

In 1996, the Tampa Bay Estuary Program (TBEP) established a Nitrogen Management Consortium of local governments, regulatory agencies and representatives of agriculture, fertilizer industries, and utility companies. This Consortium approved a plan of action to reduce each year by 17 tons the nitrogen influx to the Bay, an annual reduction that “holds the line” on nitrogen loading to Tampa Bay at $\sim$3,500 metric tons yr$^{-1}$ (TBNEP, 1996). The TBEP nitrogen management paradigm has been that reducing the total nitrogen load will effectively reduce algal blooms (chlorophyll $a$), which will improve water clarity and permit the re-establishment of sea grasses in Tampa Bay. This paradigm was based on observed and segment-specific relationships between annual nitrogen loading and chlorophyll $a$ concentrations in Tampa Bay (Pribble, et al., 2001a).

Excessive nitrogen in the form of ammonium, nitrite, nitrate and organic amine compounds stimulates the growth of algae in sunlit and quiescent surface waters (Wang, 1999). These algal mats exude noxious odors, increase water turbidity and reduce sea grass populations, and during decomposition can decrease dissolved oxygen concentrations to levels lethal to fish. The oxidation of reduced nitrogen compounds further depletes dissolved oxygen concentrations.

The TBEP estimated that direct atmospheric deposition of nitrogen to the Bay contributes between 15% and 30% of the total nitrogen loading to Tampa Bay (Pribble, et al., 2001c;
Zarbock, et al., 1996). According to Pribble, et al. (2001c) the atmospheric nitrogen delivery rate is strongly dependent on the annual rainfall, and was 790 metric tons yr\(^{-1}\) in 1996 but 1400 metric tons yr\(^{-1}\) in 1997, a year of record rainfall associated with El Niño.

For the atmospheric deposition of nitrogen, the specific research questions as defined by the Tampa Bay Estuary Program (TBEP) Tampa Bay Atmospheric Deposition Subcommittee (TBADS) were to determine and assess the

- relative contribution of various nitrogen species to nitrogen loading from deposition directly to the surface of Tampa Bay;
- relative contribution from wet vs. dry deposition;
- relationship between NO\(_x\) and ammonia, organic nitrogen, and nitric acid;
- sources of nitrogen species of concern to Tampa Bay and the relative importance of stationary, mobile and natural sources;
- fraction of nitrogen loading in stormwater delivered to the bay which originates from the atmosphere. Specifically, determine the estimated watershed transfer coefficients and retention rates of nitrogen originating as deposition to the watershed.

Monitoring of biologically-active gaseous nitric acid and ammonia, and aerosol nitrate and ammonium, began in August 1996 with the installation of ambient air and rainfall monitoring equipment at the eastern end of the Gandy Bridge. The Gandy Bridge site has been operated and maintained by the Environmental Protection Commission of Hillsborough County (EPCHC) for more than five years. Moreover, in the past two years special studies on the interaction of sea salt with nitric acid, bulk deposition of nitrogen (including organic amines), and the spatial distribution of ammonia in urban Tampa have been conducted to address the research objectives. The experimental methods adopted to determine atmospheric nitrogen deposition to Tampa Bay can be found in Appendix A and in Poor, et al. (2001).

The amount and distribution of indirect atmospheric nitrogen deposition to Tampa Bay remains an important and unanswered question, but research on this question was neither explicitly nor implicitly funded as part of the effort described in this report.

### 1.4 Role of Air Toxins

Sediments of Tampa Bay most heavily impacted by urban or commercial activities have levels of chlorinated pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), or heavy metals that in some cases pose a significant ecological or human health risk (McConnell, et al., 1996). Long and Greening (1999) reported on the toxicity of the Tampa Bay sediments based on standardized bioassays and on the chemical contamination and biological damage seen in oyster and fish tissue. The highest levels of toxicity were found in the sediments of northern Hillsborough Bay and in southeastern Boca Ciega Bay. In the most toxic sediments, the chemicals of concern were ammonia, copper, mercury, total DDTs and total PCBs. Oyster tissue from several Tampa Bay sampling sites had elevated levels of total PAHs, PCBs and chlordane; and a similar pattern was seen with PCBs and fluorescing organic compounds found in fish liver tissues. Northern Hillsborough Bay had the notoriety as the most contaminated bay segment of the Tampa Bay Estuary (Long and Greening, 1999).
The magnitude of the contaminant loading from atmospheric deposition is not well characterized. The specific research objectives for the atmospheric deposition of selected persistant, bioaccumulative and toxic compounds were to

- estimate the total (wet plus dry) annual atmospheric deposition rates;
- determine the percentage contribution of atmospheric air toxin fluxes to total fluxes to Tampa Bay;
- compare the atmospheric air toxin fluxes with atmospheric fluxes measured at national and international monitoring sites;
- apportion emissions to regional air pollution sources or source categories; and
- assess the need for control of regional source emissions.

In March 2000, sampling began at the Gandy Bridge site for ambient air concentrations of polychlorinated biphenyls (PCBs), organochlorine pesticides, and polyaromatic hydrocarbons, and ambient air and rainfall concentrations of trace metals. Appendix A describes methods of measurement and data analysis for PCBs, PAHs, pesticides and metals.
2. NITROGEN

2.1 Wet and Dry Deposition Rates

Our most recent published estimate of atmospheric deposition of inorganic nitrogen to Tampa Bay is 760 metric tons yr$^{-1}$, (Poor, et al., 2001). These estimates were based on a three-year record of ambient air and rainfall nitrogen concentrations at the Gandy Bridge site, and were corrected for the flux of ammonia-nitrogen from the bay water to the air. Ammonia/iium contributed ~60% and nitric acid/nitrate ~40% to the total annual nitrogen deposited.

Table 1 summarizes the wet and dry direct atmospheric deposition for inorganic nitrogen from August 1996 through July 2001. Roughly equal amounts of nitrogen reached the bay from wet and dry deposition. The total nitrogen deposition rates varied from 6.6 to 8.5 kg-N ha$^{-1}$ yr$^{-1}$ and were higher than the ~4 kg-N ha$^{-1}$ yr$^{-1}$ seen at more remote sites in the continental US (Sievering et al., 1996; Zeller et al., 2000), but lower than the 8-11 kg-N ha$^{-1}$ yr$^{-1}$ in the Ohio Valley and in the northeastern US (Lawrence et al., 2000).

Table 1. Annual direct atmospheric nitrogen deposition rates to Tampa Bay for inorganic ammonia/iium plus nitric acid/nitrate.

<table>
<thead>
<tr>
<th>Year (August-July)</th>
<th>Dry Wet</th>
<th>Total Dry:Wet</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kg-N/ha</td>
<td>kg-N/ha kg-N/ha</td>
</tr>
<tr>
<td>1996-1997</td>
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<td>1997-1998</td>
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<td>4.1</td>
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<td>4.1</td>
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</tr>
<tr>
<td>2000-2001</td>
<td>3.4</td>
<td>3.2</td>
</tr>
<tr>
<td>Average</td>
<td>3.9</td>
<td>3.9</td>
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</tbody>
</table>

Presented in Figures 1 and 2 are the relative contributions to dry and wet deposition, respectively, of inorganic nitric acid/nitrate and ammonia/iium nitrogen. Ammonia clearly dominates dry deposition (Figure 1), but not wet deposition (Figure 2). Figure 3 shows the relative proportions of wet and dry deposition rates by month. Both dry and wet deposition rates show a seasonal trend, with exceptions, of higher total nitrogen deposition in the summer months.
Figure 1. Monthly dry deposition of nitrogen to Tampa Bay, August 1996-July 2001.

Figure 2. Monthly wet deposition of nitrogen to Tampa Bay, August 1996-July 2001.
Figure 3. Monthly total deposition of nitrogen to Tampa Bay, August 1996-July 2001.

The assumptions behind the deposition rates reported in Table 1 are significant. First, these rates are assumed to be representative of the entire bay but based only on nitrogen ambient air and rainfall concentrations measured at the Gandy Bridge site and the meteorology over Tampa Bay south of MacDill AFB. Second, previous estimates with the NOAA buoy model have been limited to water-soluble gases. Our recent changes to the NOAA buoy model to extend its applications to partially soluble gases show that the contribution of nitrogen oxides adds another ~0.4 kg-N ha⁻¹ (or ~10%) to the dry deposition rate. Using the modeling approach of Asman, et al. (1994), however, Poor et al. (2001) have shown that the ammonia dry deposition likely overestimates by ~10% the ammonia dry flux. Third, the annular denuder system does not capture coarse particle nitrate, which is the predominant nitrate mode, thus biasing the total dry deposition estimates low (see Section 2.2 for further discussion). Finally, these estimates do not include organic forms of nitrogen.

Figure 4 illustrates the dependence of ambient air ammonia concentrations measured at the Gandy Bridge site with wind speed and direction. Such dependence may be site-specific for each pollutant and not representative of the entire bay, thus biasing the nitrogen loading rates either high or low.
NH₃ Concentration vs. Wind Speed and Direction

**Figure 4.** Average daily concentrations of ambient air ammonia as a function of wind speed and direction. Ammonia concentrations were measured with an annular denuder system over a three-year period on a 1-in-6 day schedule; average daily resultant wind speed and direction at Tampa International Airport were obtained from the National Climatic Data Center website (NCDC, 2001). Jimmy Foster, June 2001, prepared the graph.

### 2.2 Coarse Particle Nitrogen

Predominant forms of nitrogen in aerosols characteristic of the polluted air above urban settlements are ammonium sulfate and ammonium bisulfate, and ammonium nitrate. These sub-micron (~0.5 µm in diameter) particles are formed by the reactions of sulfur dioxide with ammonia and nitric acid with ammonia, respectively (Seinfeld and Pandis, 1998). The annular denuder system in operation at the Gandy Bridge site is designed to efficiently collect these fine particle aerosols. In a coastal environment, however, atmospheric sodium chloride from sea spray reacts with nitric acid to form sodium nitrate (Pakkanen, 1996; ten Brink, 1998). Sodium nitrate aerosols are typically larger than 1 µm in diameter (Ebert, et al., 2000; Mamane and Mehler, 1987), as is suggested the size distributions for sodium nitrate shown in Figure 5.

Both modeling and measurements at the Gandy Bridge site indicate that almost all of the atmospheric ammonium and nitrate is in the form of fine particle ammonium sulfate (or bisulfate) and coarse particle sodium nitrate, respectively (Campbell, et al., 2002). The annular denuder system, which has an inlet aerosol cut-point of 2.5 µm, excludes much of the coarse...
particle nitrate. Thus, our estimate of ambient air nitrate concentrations and nitrate deposition rates are biased low—how low is still the subject of current research.

Dry deposition rates are the product of the ambient air concentration of a contaminant and its deposition velocity. Using a Williams-type particle deposition model (Williams, 1982) with over-water meteorological data for Tampa Bay, deposition velocities for 0.5-µm and 5-µm diameter particles typical of ammonium sulfate and sodium nitrate are 0.008 cm s⁻¹ and 0.08 cm s⁻¹, respectively, a factor of 10 different, and lower than the average deposition velocity of 0.1 cm s⁻¹ applied in the recent NOAA buoy model estimates of Poor, et al. (2001).

Although no long term coarse particle nitrate data exist for the Gandy Bridge site, short-term intensive campaigns described by Campbell, et al. (2002) and Evans, et al. (2001) suggest that the average dry deposition rate to Tampa Bay of coarse particle nitrate is between 10 and 100 metric tons yr⁻¹. In Figure 5 can be seen two coarse particle modes, one at ~5 µm and one at ~10 µm. If the ~10 µm mode is not a sampling artifact (Evans and Poor, 2002), then the coarse particle nitrate deposition will be closer to 100 metric tons yr⁻¹ than 10 metric tons yr⁻¹.

**Figure 5.** Size distributions for sodium, chloride and nitrate collected at the eastern end of the Gandy Bridge from October to November 2001. Backwards air mass trajectories computed with the NOAA HYSPLIT model (NOAA, 2001) showed (a) marine, (b) mixed marine and terrestrial, and (c) terrestrial wind origins.
2.3 Organic Nitrogen

Atmospheric wet and dry deposition of nitrogen can be directly measured with an open collector, for example, an open bucket. Historically open buckets or funnels received not only the unknown fraction of dryfall or wetfall of interest, but also bird droppings, frog feces, bugs, and other unwanted debris, which contaminated the sample. Thus, the opinion of many scientists including participants on the Tampa Bay Atmospheric Deposition Subcommittee (TBADS, 2001) is that bulk deposition samples are synonymous with contaminated samples. If contamination could be avoided, bulk deposition sampling might offer an easy and relatively inexpensive method of quantifying nitrogen compounds that coat the collector surface.

On behalf of the Tampa Bay Estuary Program, the EPCHC deployed a bulk deposition sampler at the Gandy Bridge from May 1999 to December 2000 to evaluate the efficacy of such a method. The bulk collector consisted of a 12.2-cm diameter polycarbonate funnel attached to a 2-L polyethylene bottle via Teflon tubing. The collector was installed on a pole ~3 m above the ground, with fishing line around the funnel to prevent birds from landing. Later the pole was greased to prevent frogs from climbing into the funnel. The collector was removed and replaced weekly, and the rinseate from funnel along with any rainwater in the bottle were analyzed for total Kjeldahl nitrogen (TKN) and nitrate. Ammonium was not measured, thus a direct comparison with the wet and dry ammonia/ium deposition rates could not be made.

Direct deposition (i.e., bulk collector) rates were ~20% higher than the rates calculated using the NOAA buoy model to infer dry deposition plus direct wet deposition, with ~30% of the bulk collector data eliminated due to obvious signs of contamination. We theorized that the higher direct deposition rate may be a consequence of (1) dry depositing sodium nitrate (see Section 2.2 for discussion of sodium nitrate), and (2) organic nitrogen in both dryfall and rainfall, as TKN includes inorganic ammonium plus organic amines. Scudlark, et al. (1998), estimated that on an annual basis, ~20% of the nitrogen in rainfall along the mid-Atlantic US coast is organic nitrogen.

To pursue this line of reasoning, we re-deployed the bulk deposition collector at the eastern end of the Gandy Bridge, but at a newly constructed and temporary site. The bulk collector was removed and replaced daily, and with this sampling frequency no samples had evidence of contamination. TKN and ammonium were analyzed in the funnel rinseate and in the rainwater (when present). Organic nitrogen was computed as the difference between the TKN and ammonium nitrogen, less the nitrogen measured in laboratory or field blanks. For a month-long sampling period, daily direct deposition of organic amine nitrogen and ammonium nitrogen revealed that of the estimated ~0.01 kg-N ha\(^{-1}\) d\(^{-1}\) the organic nitrogen was the larger fraction (~70%), which would represent a ~300 metric ton yr\(^{-1}\) increase in the earlier estimate of nitrogen deposition to Tampa Bay if this rate were consistent throughout the year (Figure 6).

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2 The Gandy Bridge monitoring site is wholly within a Marine Corps Reserve training facility. In the weeks that followed the September 11, 2001, terrorist attack that destroyed the World Trade Center, access to the Gandy Bridge site was restricted to all but essential personnel. Courtesy of the Florida Fish and Wildlife Conservation Commission, a temporary research site was constructed on the south side of Gandy Boulevard and adjacent to the city park.
We suspect that the organic amines are predominantly methylamines associated with marine air (Van Neste, et al., 1987), but other sources include suspended soils and pollen, and emissions from animal feedlots, incineration and wastewater treatment. Scudlark, et al. (1998) postulated that terrestrial sources and not seawater were the source of the organic nitrogen in their samples.

![Graph showing atmospheric deposition rates of organic amine nitrogen and ammonium nitrogen in bulk deposition samples collected at a bayside site in Tampa, Florida. These rates include days with and without rainfall (Hendrix, et al., 2002).](graph.png)

**Figure 6.** Atmospheric deposition rates of organic amine nitrogen and ammonium nitrogen in bulk deposition samples collected at a bayside site in Tampa, Florida. These rates include days with and without rainfall (Hendrix, et al., 2002).

Daily ammonia gas and ammonium aerosol concentrations obtained from an annular denuder system were collocated with the direct deposition measurements of TKN and ammonium. Deposition velocities were calculated with the NOAA buoy model and the Williams model for gases and aerosols, respectively, with meteorological data obtained from local sensors. The size distribution of ammonium, which is needed to calculate the aerosol deposition velocity, was determined from collocated three-day integrated and size-speciated ambient air concentrations made with an Anderson cascade impactor (Evans, et al., 2001; Hendrix, et al., 2001).

Comparing the bulk ammonia nitrogen flux for collocated samples on days with no rainfall, the bulk ammonia flux was ~50% lower than the ammonia predicted by the inferential model, and the daily fluxes were not significantly correlated, as shown in Figure 7 (Hendrix et al., 2002). An explanation for this result is that ammonia gas is not quantitatively trapped on the funnel surface.
2.4 Spatial Gradient of Ammonia Across Urban Tampa

In the industrial parks and ports adjacent to Tampa Bay, ammonia and ammonium fertilizer are commodities, routinely traded between ship and shore. Nitric acid and ammonium fertilizer are manufactured at facilities close to the bay. Also proximate to the bay are large refrigeration companies that use ammonia for cooling, and a 50 MGD (million gallons per day) municipal wastewater treatment plant receiving ammonium-rich influent wastewater. Figure 8 and Table 2 identify the activities close to Hillsborough Bay.

In this past decade, ammonia emissions from late model vehicles have increased markedly, and researchers postulate that this increase is related to inefficiencies in the 3-stage catalytic converters, which are designed to convert nitrogen oxides to inert nitrogen (Fraser and Cass, 1998). Under non-ideal engine performance conditions (for example, high speeds) nitrogen oxides may be reduced to ammonia (Durbin, et al., 2002). Heavily traversed freeways crisscross Tampa Bay, thus ammonia and nitrogen oxide emissions from cars and trucks may have a disproportionate impact on the bay.
Our goals in surveying the ambient air ammonia concentrations in urban Tampa were to

- test a passive sampling device for ammonia sampling over large geographical areas,
- characterize the ammonia concentration gradients adjacent to the bay for representative land uses, and
- identify any un-inventoried “hot spots.”

Method development and testing took the prior full year, but in October 2001 more than 90 passive sampling devices (PSDs) spaced ~1.5 km apart were simultaneously deployed for two weeks in central Tampa, in an area bounded on the north by Interstates 4 and 275, including the locally famous “malfunction junction,” to the east by Interstate 75, to the south by the Gibsonton, and to the west by Tampa Bay. On the southern Tampa peninsula, PSDs were placed south to Bay-to-Bay Boulevard (Tate, 2002). Within the regional coverage were suburbs, an urban center, major highways, port activities, fertilizer manufacturing, wastewater treatment, coal-combustion power plants, warehousing and dairy farming.

Using kriging as a technique for spatial interpolation, Tate (2002) plotted the ammonia concentration contours, as can be seen in Figure 8. Not surprisingly, these contours ring all but one of the largest known ammonia emission sources (Table 2). An ammonia plume or gradient along the major transportation corridors is not evident (Figure 8). Ammonia concentrations in the vicinity of the Cargill fertilizer operations were not above background. Tate offered three plausible explanations: first, the predominant winds were from the north to northeast, which would tend to push any plume out over the bay; second, sulfur dioxide and sulfuric acid emitted from the fertilizer operations would react with ammonia to form aerosol ammonium sulfate; and third, the large phospho-gypsum stacks to the north and northeast of the plant would act as a huge sink for ambient air ammonia, which is consistent with the contour plot (Figure 8).

What constitutes a “high” ammonia concentration? With respect to human health, no National Ambient Air Quality Standard for ammonia exists; the State of Florida guideline for an acceptable ambient air concentration is 360 µg m⁻³ based on an 8-hour average (ATSDR, 2002); and the OSHA permissible workplace concentration is 35,000 µg m⁻³. The odor threshold for ammonia is ~17,000 µg m⁻³, which would represent a nuisance concentration if not a health threat.

With respect to environmental health, excessive ammonia in air and water favors algal growth, and a build-up of water-dissolved ammonia/ium is toxic to fish. Sediments serve as a reservoir for reduced nitrogen, which can be released to the water column under conditions that favor mixing (for example, cooler surface temperatures or high winds). The task of defining an ambient air concentration of ammonia protective of environmental health is made difficult by the ability of an estuary to store and recycle nitrogen.

Typical ambient air concentrations of ammonia measured at ground level are ~0.1 to 4 µg m⁻³ (ATSDR, 2002; Sutton, et al., 1994), in agreement with this study, but concentrations over animal feedlots and freshly fertilized fields may exceed 100 µg m⁻³. We have measured average daily ammonia concentrations of ~1000 µg m⁻³ next to the lime stabilization sludge treatment process at a Pasco County facility and at an Oldsmar wastewater treatment plant (Mower, 2002).
These elevated ammonia concentrations dropped to ambient levels within a few hundred meters of the process.

For most of the PSD coverage, 2-week averaged ammonia concentrations were at background concentrations of 1-2 µg m\(^{-3}\), with a peak of 16 µg m\(^{-3}\) next to Port Sutton Road. Under low wind conditions, the plume of ammonia from the Port of Tampa may reach the Gandy Bridge site, albeit at diluted concentrations (Figure 8). The relatively steep concentration gradients and low ambient air concentrations of these “hot spots” do not indicate a major impact to Tampa Bay as a whole, but represent a potential impact to Hillsborough Bay. The local impact of the ammonia plumes on Hillsborough Bay may be mitigated by atmospheric dispersion and by the bi-directional flux of ammonia across the air/water interface, which is discussed in the next section.

**Table 2.** Inventoried ammonia emission sources near Hillsborough Bay (TRI, 2001; CMU 2001).

<table>
<thead>
<tr>
<th>Map Number</th>
<th>Name</th>
<th>Emissions 1000 kg yr(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nitram</td>
<td>160</td>
</tr>
<tr>
<td>2</td>
<td>Howard F. Curren Waste Water Treatment Plant</td>
<td>150</td>
</tr>
<tr>
<td>3</td>
<td>Cargill Fertilizer-Riverview Operations</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>IMC AGRICO – Port Sutton Terminal</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>Farmland Hydro L P – Ammonia Terminal</td>
<td>17</td>
</tr>
<tr>
<td>6</td>
<td>AMERICOLD - Tampa</td>
<td>14</td>
</tr>
<tr>
<td>7</td>
<td>CF Industries – Ammonia Terminal</td>
<td>13</td>
</tr>
<tr>
<td>8</td>
<td>Reddy Ice - Tampa</td>
<td>3.9</td>
</tr>
<tr>
<td>9</td>
<td>Coca Cola Bottling - Tampa</td>
<td>3.5</td>
</tr>
<tr>
<td>10</td>
<td>Trademark Nitrogen</td>
<td>2.0</td>
</tr>
<tr>
<td>11</td>
<td>Harborside Refrigerator Services</td>
<td>1.9</td>
</tr>
<tr>
<td>12</td>
<td>AMERICOLD - Port</td>
<td>0.91</td>
</tr>
<tr>
<td>13</td>
<td>UNIROYAL Optoelectronics</td>
<td>0.68</td>
</tr>
<tr>
<td>14</td>
<td>Rapid Blueprint</td>
<td>0.43</td>
</tr>
</tbody>
</table>
Figure 8. Two-week averaged ammonia concentration gradient across urban Tampa, October 2001 (Tate, 2002). The numbers indicate inventoried ammonia emission sources, as described in Table 2. Units for the color scale are µg/m³.
Figure 9. USGS aerial photograph of Hooker’s Point, Tampa, showing the deep-water ports and industrial complexes. In the months prior to deployment of the PSD network, preliminary or “scoping” ammonia concentration measurements were made by PSD at 4 sites on Hooker’s Point: (S) adjacent to Howard Curran wastewater treatment plant sludge drying beds; (R) next to the railway conveyance for product transfer; (F, D) close to the docks.

According to Tate (2002), weekly average ammonia concentrations made by PSD at several sites on Hooker’s Point prior to deployment of the PSD network were as high as 180 $\mu$g m$^{-3}$ at the fence line next to the sludge drying ponds of the Howard F. Curran wastewater treatment plant, and 150 $\mu$g m$^{-3}$ at the railcar transfer facility, which was downwind of the sludge drying beds (Figure 8, S and R, respectively). This ambient air concentration equates roughly to an ammonia emission rate of ~1 metric tons d$^{-1}$, a substantial release even if for a few weeks. No sludge was present in the drying beds during the PSD deployment in October 2001.

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$^3$ Based on air dispersion modeling with CALMET/CALPUFF of a ground-based ammonia release, described at [http://www.hsc.usf.edu/publichealth/EOH/BRACE/DepositionRate.html](http://www.hsc.usf.edu/publichealth/EOH/BRACE/DepositionRate.html); research in progress will compare air dispersion modeling of the ammonia emissions with the PSD ammonia measurements around Hillsborough Bay.
2.5 Bi-Directional Ammonia Flux at the Air/Water Interface

With ambient air ammonia concentrations of 1-2 µg m\(^{-3}\), increases in bay water salinity, pH, temperature or ammonium concentration favor the evasion of ammonia from the water to the air not only in Tampa Bay (Poor, et al., 2001), but also in the Chesapeake Bay (Larsen, et al., 2001). Thus, the bay water may be both a source and a sink for ammonia.

To better understand the temporal cycle of the bi-directional ammonia flux, Mizak and Poor (2002) made coincident daily measurements of air and water ammonia/ium concentrations along with water quality parameters off of a seawall at the Gandy Bridge monitoring site. For three days of a 6-day pilot study, January 11-12, 2002, conditions favored ammonia evasion, based on the calculational approach of Asman, et al. (1994). Typical ammonium bay water concentrations near Gandy Bridge are ~0.02 mg/L, however, during this measurement period concentrations were as high as 0.4 mg/L. The higher ammonium concentrations in the bay were thought to be a result of a dispersed plume of process water,\(^4\) discharged to Bishops Harbor in November to December 2001, as illustrated in Figure 10.

Additional pilot studies are in progress to devise an optimal sampling strategy for intensive over-water monitoring of air and water ammonia/ium concentrations. Both the Florida Department of Environmental Protection under BRACE, and a recently awarded grant from the University of Florida Water Resources Research Center fund this research.

2.6 Sources of Ambient Air Nitrogen

We have tried several approaches to apportion the sources of nitric acid, ammonia, and ammonium and nitrate aerosols to Tampa Bay, with limited success. By inventory, power plants and mobile vehicles are the two largest source categories for nitrogen oxide emissions, both nationally and locally (USEPA, 2001; USEPA, 1998). Ammonia releases, however, have been reported primarily through the Toxic Release Inventory (TRI, 2001), which does not include releases from the many relevant source categories such as intensive livestock farming or fertilizer application. Carnegie Mellon University has made available at their website an emissions factor program by which local ammonia emissions can be estimated (CMU, 2001). From the Carnegie Mellon emission factors, the TRI, and the USEPA national inventory, we estimated that the 2000 ammonia emissions for Pinellas and Hillsborough County totaled ~8,000 metric tons yr\(^{-1}\), distributed between the source categories as shown in Figure 11.

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\(^4\) In October 2001, to prevent a catastrophic collapse of the elevated containment ponds, the state authorized 68 million gallons of partially treated process water from Piney Point phosphate plant to be discharged into Tampa Bay. "The effects of such an event [collapse of ponds] would be devastating to the ecosystem, would create a risk to the public health and welfare, and would result in severe property damage," according to an emergency order issued in September by the Florida Department of Environmental Protection. --from *The Tampa Tribune* Nov 21, 2001
Figure 10. Plot of ammonium nitrogen in Tampa Bay for January 2002. Graphic is courtesy of the Environmental Protection Commission of Hillsborough County.
Figure 11. Ammonia emissions by source category for Pinellas and Hillsborough County. The inventory was assembled by Connie Mizak, June 2001, with data from CMU (2001), the TRI (2001) and the USEPA (2001); and updated by Scott Mower, February, 2002.

For both nitric acid and ammonia, we looked at the wind dependence of ambient air concentrations measured at the Gandy Bridge site; stable nitrogen isotope ratios in rainwater and fine particle aerosols; air mass trajectories and chemical composition of rainfall; and for nitrogen oxides nitrogen release simulations with the CALMET/CALPUFF modeling system.

Although ambient air concentrations of ammonia at the Gandy Bridge site were higher for easterly winds and low wind speeds (Figure 4), no such directional dependence was seen for nitric acid (Figure 12). To some extent, this was an expected result because nitric acid forms from nitrogen oxides in the atmosphere through a series of coupled photochemical and chemical reactions that may take hours to days to complete. Another interpretation of Figure 12, however, is that on calm days, regional nitrogen oxide emissions from motor vehicles had time to partially transform to nitric acid, thus yielding higher nitric acid concentrations at the Gandy Bridge site (and most likely across the urbanized Hillsborough and Pinellas Counties). Directly south of
Gandy Bridge site is more than 20 km of open water, which explains the lower nitric acid concentrations in only that direction.

**HNO₃ Concentration vs. Wind Speed and Direction**

![HNO₃ Concentration vs. Wind Speed and Direction](image)

**Figure 12.** Average daily concentrations of ambient air nitric acid as a function of wind speed and direction. Nitric acid concentrations were measured with an annular denuder system over a three-year period on a 1-in-6 day schedule; average daily resultant wind speed and direction at Tampa International Airport were obtained from the National Climatic Data Center website (NCDC, 2001). Jimmy Foster, June 2001, prepared the graph.

We simulated with the CALMET/CALPUFF modeling system the release of nitrogen oxides from the largest stationary sources and from mobile sources, with the intent to provide a deposition factor that would relate the emissions from these source categories to the resulting wet and dry deposition of nitric acid and nitrate to Tampa Bay. A description of the CALMET/CALPUFF modeling system, its parameterization for the simulations, and justification for the 400 km x 390 km size of the modeling domain are given in Venegas, et al. (2001).

The Tampa Electric Company (TECO) Big Bend and Gannon power plants combined emitted 59,000 tons of nitrogen oxides in 2000, ~40% of the total nitrogen oxide emissions inventory for Hillsborough and Pinellas Counties. Hourly emission rates from each of the plant stacks as well as the stack physical characteristics were obtained from the USEPA emission inventory website (USEPA, 2001). Mobile sources were modeled as 43 volume sources over major transportation arteries; and the 42,000 tons of mobile source emissions were divided proportionally between each volume source according to traffic counts.
Using the meteorological data for April 2000 in the CALMET/CALPUFF model system, we modeled the transport, dispersion, transformation and (wet plus dry) deposition to Tampa Bay of nitrogen oxide emissions from the TECO, Inc., power plants and from motor vehicles in Hillsborough and Pinellas County. The CALMET portion of the model created a three-dimensional diagnostic wind field over the modeling domain, which we visualized in time and space (i.e., four dimensions) with the Environmental Workbench software developed by SESSCO, Inc. This allowed us to easily review the wind fields and compare modeled with actual winds. The CALPUFF portion of the model predicted through a pseudo-linear empirical model the transformation of nitrogen oxide to nitric acid. The transformation rate depends on sulfur dioxide and ozone concentrations; the former is modeled from emissions data and the latter is input from regional monitors. The CALPUFF algorithms also predict from thermodynamic considerations the partitioning of nitric acid to nitrate. This partitioning depends on sulfate concentration (modeled), ammonia concentration (input as an annual average), temperature and relative humidity (input as hourly averages).

Early simulations with CALPUFF gave nitrogen oxide deposition velocities that were unusually high compared with values found in Seinfeld and Pandis (1998), for example. To solve this problem, the integrated NOAA buoy/Williams model was modified to include the transfer of a partially soluble gas from the atmosphere to the water. The NOAA buoy model was then run with April 2000 meteorological data and from the output a diurnal deposition velocity profile was developed for nitrogen oxide, nitrogen dioxide, and nitric acid and nitrate. These deposition velocity profiles were then input into the CALPUFF model for the deposition rate calculations.

Based on this one month of CALMET/CALPUFF modeling, the estimated deposition factors are ~1800 and ~320 metric tons of nitrogen oxide emitted for each ton of nitrogen directly deposited to Tampa Bay, for the TECO power plants and motor vehicles, respectively. This translates into ~30 metric tons yr\(^{-1}\) from the TECO power plants and ~130 metric tons yr\(^{-1}\) from motor vehicles. Recall that Poor et al. (2002) estimated that ~300 metric tons yr\(^{-1}\) of oxidized nitrogen deposited from the atmosphere to Tampa Bay. If the remaining stationary and area sources of nitrogen oxides were included in the CALPUFF modeling, the agreement between modeled and measured deposition would be reasonable. Although we continue to improve the CALMET/CALPUFF-generated deposition factors, our initial results support the conclusion that mobile source emissions contribute disproportionately more nitrogen to the bay than the TECO power plant emissions.

Earls (2001) examined the trends and source apportionment of nitrogen in rainfall and ambient air using the stable isotope measurements \(^{15}\text{N}\), which were expressed as \(\delta^{15}\text{N}\), the enrichment or depletion of \(^{15}\text{N}\) relative to clean air (Equation 4, Appendix A). Refer to Appendix A for details of the sampling and laboratory analyses. Data analyses included summary statistics and histograms of the \(\delta^{15}\text{N}\) data; graphical analyses of \(\delta^{15}\text{N}\) data by rainfall nitrate and ammonium

\(^5\) Dr. Venkat Bhethanabotla has integrated the Williams particle deposition model with the NOAA buoy model to improve the particle deposition velocity calculations; moreover, he has modified the NOAA buoy model for insoluble gas transfer at the air/water interface. The model description and instructions for use are at www.eng.usf.edu/~bhethana/.
and ambient air particulate nitrogen concentrations, wind direction, and air mass trajectory origin; and correlations with rainfall and ambient air pollutants.

The average $\delta^{15}N$ values for rainfall and ambient air at the Gandy Bridge monitoring sites are summarized in Table 3, which is also organized by a wet and dry season. The results did not suggest a strong seasonal difference $\delta^{15}N$ values, but evident is a slight shift toward more enriched values during the rainy season. Strongly enriched $\delta^{15}N$ values were associated with a few isolated events such as a tropical storm.

**Table 3.** Statistics for precipitation (rain) $\delta^{15}NH_4^+$ and $\delta^{15}NO_3^-$ and ambient air (dry) total $\delta^{15}N$ observations for complete datasets and by wet and dry seasons, reported in ‰ (per mil), n = number of samples in each category. Dry season was defined as October through May and wet season as June through September. Sampling was done at the Gandy Bridge monitoring site in Tampa, Florida.

<table>
<thead>
<tr>
<th>$\delta^{15}N$ Observations</th>
<th>Mean</th>
<th>Std Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rainfall Data</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>July 1998 to November 1999 (n=88)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{15}NH_4^+$</td>
<td>-4.9</td>
<td>4.2</td>
</tr>
<tr>
<td>$^{15}NO_3^-$</td>
<td>-1.8</td>
<td>3.8</td>
</tr>
<tr>
<td>Dry Season (n=23)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{15}NH_4^+$</td>
<td>-5.9</td>
<td>3.0</td>
</tr>
<tr>
<td>$^{15}NO_3^-$</td>
<td>-3.1</td>
<td>3.8</td>
</tr>
<tr>
<td>Wet Season (n=65)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{15}NH_4^+$</td>
<td>-4.6</td>
<td>4.6</td>
</tr>
<tr>
<td>$^{15}NO_3^-$</td>
<td>-1.4</td>
<td>3.7</td>
</tr>
<tr>
<td><strong>Ambient Air Data</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>February 1999 to November 1999 (n=47)</td>
<td>-0.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Dry Season $^{15}N$ (n=18)</td>
<td>-0.8</td>
<td>2.7</td>
</tr>
<tr>
<td>Wet Season $^{15}N$ (n=29)</td>
<td>-0.1</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Significant shifts in $\delta^{15}N$ values were seen when data were arranged by air mass trajectory, as illustrated by Table 4. The name of the trajectory indicates its direction of travel relative to Tampa. For example, the Cuba trajectory represents an air mass that traveled across Cuba and up the west coast of Florida, approaching Tampa from the south.

Literature values of oxidized nitrogen $\delta^{15}N$ range from −1 to +5‰ for fuel nitrogen, −5 to +5‰ for pollution nitrogen oxides, −15 to −5‰ for clean nitrogen dioxide, and +6 to +12‰ in coastal rainfall (Freyer, 1978; Heaton, 1986). Combustion processes that produce nitrogen oxides, which are transformed into nitric acid and nitrate, contribute little to the enrichment or depletion of $\delta^{15}N$ (Heaton, 1986). As compiled in Table 4 for monitoring at the eastern end of Gandy Bridge, nitrate $\delta^{15}N$ ($\delta^{15}NO_3^-$) values that approached zero were correlated with higher nitrate rainfall and ambient air particulate nitrogen concentrations, which suggest combustion sources with air mass trajectories for Atlanta, Cuba and Tampa. One caveat on this interpretation is that on a few days, rainfall that occurred when an air mass approached from the direction of Cuba had the
most positive nitrate $\delta^{15}$N values and the lowest nitrate concentration. The occurrence of these events affected the overall average for the Cuba trajectories.

Literature values of ammonia $\delta^{15}$N range from $-15$ to $-5\%$ for barnyard air, $-10$ to $+1\%$ for coal combustion, $-3$ to $+2\%$ for ammonia production, $-5$ to $0\%$ for fertilizer use and $+3$ to $+18\%$ in coastal rainfall (Freyer, 1978; Heaton, 1986). For ammonia, strongly depleted $\delta^{15}$N values have been previously linked with ammonia volatilization from organic fertilizers, wastewater treatment, and animal urea, as examples (Heaton, 1986). The most depleted $\delta^{15}$N for rainfall ammonium or ambient air particulate nitrogen were associated with trajectories from the Bahamas and Atlanta, and from the Gulf and Bahamas, respectively (Table 4). The most dramatic difference is seen in the $-1.0$ average $\delta^{15}$NH$_4^+$ for a possibly cleaner air mass that arrives over Tampa Bay directly south from Cuba versus the $-7.8$ average $\delta^{15}$NH$_4^+$ for an air mass that has passed over the Miami metropolitan area and came across south central Florida before reaching Tampa Bay.

Table 4. Statistics for precipitation $\delta^{15}$NH$_4^+$ and $\delta^{15}$NO$_3^-$ and ambient air total $\delta^{15}$N for each trajectory class, reported in $\%$ (per mil), $n =$ number of samples in each category. Sampling was done at the Gandy Bridge monitoring site in Tampa, Florida.

<table>
<thead>
<tr>
<th>Trajectory (Rain)</th>
<th>Avg. $\delta^{15}$NH$_4^+$</th>
<th>Avg. $\delta^{15}$NO$_3^-$</th>
<th>Trajectory (Dry)</th>
<th>Avg. $\delta^{15}$N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cuba (n=15)</td>
<td>-1.0</td>
<td>0.1</td>
<td>Atlanta (n=5)</td>
<td>0.7</td>
</tr>
<tr>
<td>Gulf (n=13)</td>
<td>-3.5</td>
<td>-1.5</td>
<td>Cuba (n=4)</td>
<td>0.6</td>
</tr>
<tr>
<td>Tampa (n=12)</td>
<td>-4.5</td>
<td>-0.9</td>
<td>Tampa (n=4)</td>
<td>0.6</td>
</tr>
<tr>
<td>Panhandle (n=10)</td>
<td>-5.2</td>
<td>-3.1</td>
<td>Cape (n=13)</td>
<td>-0.6</td>
</tr>
<tr>
<td>Cape (n=16)</td>
<td>-6.1</td>
<td>-3.5</td>
<td>Panhandle (n=5)</td>
<td>-0.9</td>
</tr>
<tr>
<td>Atlanta (n=3)</td>
<td>-6.3</td>
<td>-0.1</td>
<td>Bahamas (n=7)</td>
<td>-1.0</td>
</tr>
<tr>
<td>Bahamas (n=19)</td>
<td>-7.8</td>
<td>-2.3</td>
<td>Gulf (n=9)</td>
<td>-1.4</td>
</tr>
</tbody>
</table>

Smith et al. (2001) looked for trends of nitrate and ammonium concentrations in 293 daily rainfall samples taken at the Gandy Bridge site from August 1996 through December 2000, measurements that are part of the NOAA AIRMoN program (NADP, 2001). Keeping an air mass trajectory classification similar to that described by Earls (2001), Smith et al. (2001) noted that consistent with the $\delta^{15}$N data ammonium and nitrate rainwater concentrations and wet deposition fluxes (Figure 13) were lower for an air mass that crossed over water prior to reaching the Tampa metropolitan area; and higher for an air mass that was stagnated over Tampa.

More than 50% of the rainfall events were related to the arrival of a marine air mass, and only 8% occurred for a Tampa (or weak local flow) air mass. Moreover, even the “cleanest” rainfall contained a significant amount of inorganic nitrogen. The implication is that much of the nitrogen in the rainfall may be transported from outside the immediate Tampa Bay area.
Figure 13. Rainwater concentrations (top) and nitrogen wet deposition rates (bottom) by air mass trajectory for nitrate and ammonia (Smith, et al., 2001). Analyzed were 293 daily rainfall samples collected at the Gandy Bridge site from August 1996 to December 2000. Trajectories were obtained from the NOAA HYSPLIT website (http://gus.arlhq.noaa.gov/ready/hysplit4.html).
2.7 Summary

To summarize our understanding of the atmospheric deposition of nitrogen to Tampa Bay:

- Our best estimate is ~800 metric tons yr\(^{-1}\): ~400 metric tons yr\(^{-1}\) from dry deposition and ~400 metric tons yr\(^{-1}\) from wet deposition; ~500 metric tons yr\(^{-1}\) from ammonia/ium and ~300 metric tons yr\(^{-1}\) from nitric acid/nitrate;
- Organic amines are present in significant quantities in the dryfall and wetfall from the atmosphere, and they may contribute to the total nitrogen loading;
- Dry deposition rates are controlled by regional nitrogen emissions, but wet deposition likely has a substantial amount of transported nitrogen, based on wind sector/trajectory analyses;
- Ammonia “hot spots” near Tampa Bay likely contribute to an ammonia plume that extends over the Hillsborough Bay under low wind conditions, and the bay itself may be a source of atmospheric ammonia; and
- Air dispersion modeling indications that mobile vehicle nitrogen oxide emissions contribute more nitrogen directly to Tampa Bay than do the emissions from the large coal-fired power plants.

As a part of the Bay Regional Atmospheric Chemistry Experiment (BRACE), researchers will look at the total nitrogen budget with near-real time measurements at three sites along the predominant northeasterly wind direction as well as from an aircraft transiting the urban plume. Extensive organics and metals monitoring will better elucidate the relationships between atmospheric nitrogen and its emission sources, and perhaps identify the best source “tracer” compounds for long-term monitoring. High-speed temperature and 3-dimensional wind measurements at a station in the bay will help characterize the atmospheric turbulence over the water and thus improve gas and aerosol deposition velocities. Urban airshed modeling with a state-of-the-art full photochemical and aerosol model, run on a 2-km grid scale and initialized and validated with high quality ambient air concentration data will accomplish the nitrogen source apportionment that has thus far eluded us.

2.8 Recommendations

The ambient air and rainfall concentrations of inorganic nitrogen and the direct atmospheric nitrogen flux to Tampa Bay represents a moderate but clearly anthropogenic impact on the health of the estuary. Not yet developed are techniques to qualitatively capture and quantify the nitrogen compounds of interest, not adequately characterized are regional nitrogen emissions, especially from non-point sources, and not fully understood are all of the pathways between emissions and deposition. Gone is the naiveté that this is an easy or even a finite task.

We recommend that the Tampa Bay Estuary Program:

- Support at a minimum the long-term operation of an AIRMoN site at the eastern end of Gandy Bridge to identify trends in nitrogen deposition that are likely to accompany population growth, not only in the Tampa Bay metropolitan area but across Florida.
- Conduct an inventory of nitrogen emissions to the atmosphere from wastewater.
treatment, including sludge processing and power generation, for 10 MGD or larger facilities situated within 2 km of Tampa Bay.

✔ Find a way to measure the indirect atmospheric deposition component of total nitrogen loading to Tampa Bay.

✔ Encourage interdisciplinary and cooperative studies that integrate air, water, sediment and biota measurements and data analyses, for example, the partitioning or exchange of ammonia, organic amines, and nitrogen oxides between these media.

✔ Establish or adopt a framework for interpreting the impact of atmospheric nitrogen deposition on the health of Tampa Bay.
3. AIR TOXINS

3.1 Polychlorinated Biphenyls (PCBs)

PCBs have been found in the sediments of Hillsborough Bay, McKay Bay, Boca Ciega Bay, and Old Tampa Bay at concentrations in the range of 0.01 to 2.4 mg kg\(^{-1}\), and at these concentrations the bioaccumulation of PCBs may pose a risk to osprey and in some cases, humans (McConnell, et al., 1996). Earlier loading rate estimates accounted for 11.2 kg yr\(^{-1}\) solely from atmospheric deposition (Frithsen, et al., 1995).\(^6\) None of the PCB congeners listed in Table 5 were found in the ambient air at total (particle plus gas) concentrations above the analytical method lower detection level. Thus, a PCB flux gradient if present is likely from the sediments to the water and the water to the air.

Ambient air concentrations of total PCBs reported by Park, J., et al. (2001) for a 1995-1996 study in Galveston, Texas, were in the range of 0.21-4.9 ng m\(^{-3}\), with an average concentration of 1.2 ng m\(^{-3}\); within this range, the highest concentrations were measured for vapor phase trichlorinated and tetrachlorinated PCBs (PCB-28 through PCB-101). Rainfall concentrations were in the range of 0.08-3.3 ng l\(^{-1}\) and 0.05-2.2 ng l\(^{-1}\) for dissolved and particulate PCBs, respectively, and Park, J., et al. (2001) reported a total PCB wet plus dry flux of 6.4 µg m\(^{-2}\) yr\(^{-1}\) directly to the surface of Galveston Bay. This flux translates into a loading rate of 9.2 kg yr\(^{-1}\) to Galveston Bay. The net flux over Galveston Bay, however, was 78 µg m\(^{-2}\) yr\(^{-1}\) and from the water to the air (Park, J., et al., 2001).\(^7\)

A summary of air toxin deposition rates to the Great Lakes for data collected between 1988-1994 had across five monitoring sites annual mean total PCBs vapor phase concentrations of 0.09-0.36 ng m\(^{-3}\), particulate concentrations up to 0.009 ng m\(^{-3}\), and rainfall concentrations of 0.7-3.1 ng l\(^{-1}\) (Hoff, et al., 1996). For 1994, these PCB concentrations translated into total PCB wet plus dry fluxes of 1.4 µg m\(^{-2}\) yr\(^{-1}\), 3.4 µg m\(^{-2}\) yr\(^{-1}\), 1.2 µg m\(^{-2}\) yr\(^{-1}\), 3.0 µg m\(^{-2}\) yr\(^{-1}\), 1.0 µg m\(^{-2}\) yr\(^{-1}\) for Lakes Erie, Ontario, Michigan, Huron and Superior, respectively. For all of these lakes the net flux was from water to air and ranged from 15 to 45 µg m\(^{-2}\) yr\(^{-1}\).

The approach of Hoff, et al. (1996) and Park, J., et al. (2001) for calculating the net flux of PCBs across the air/water interface is similar to the approach described in Appendix A (Equations 7 – 19), but included measured PCB concentrations for water and for gas and particle fractions in the atmosphere.

The average PCB congener concentrations measured in the vicinity of the Great Lakes were ~the lower detection levels (LDLs) for the method employed to monitor PCBs at the Gandy Bridge site in Tampa, Florida. If we apply an average wet plus dry deposition rate of 2.0 µg m\(^{-2}\) yr\(^{-1}\) to Tampa Bay, the loading rate is ~2.1 kg yr\(^{-1}\). The ambient air PCBs concentrations measured in near Galveston Bay, Texas, were higher than those reported in Table 3 as LDLs, but the climate and geography have more in common with Tampa Bay than with the Great Lakes. If Tampa Bay had a PCB loading rate similar to Galveston Bay, the annual loading would be 6.6 kg yr\(^{-1}\), which is ~60% of the original

\(^6\) Frithsen et al. (1995) describes the primary source of PCBs in Tampa Bay sediments as leaks and spills of PCB-containing fluids, however, they make no estimate of this non-point source loading due to insufficient data.

\(^7\) Multiply µg m\(^{-2}\) yr\(^{-1}\) by 10\(^{-5}\) to convert to kg ha\(^{-1}\) yr\(^{-1}\). The surface of Tampa Bay is ~10\(^5\) ha.
Persistent, bioaccumulative or toxic pesticides discovered in the sediments of the Tampa Bay Estuary at concentrations that may pose a risk to aquatic or avian species include chlordane, dieldrin, DDT, DDE and lindane (McConnell, et al., 1996). Frithsen, et al. (1995) employed the geometric mean of Florida rainfall concentration data reported in literature to estimate the direct deposition of these pesticides from the atmosphere to the Tampa Bay Estuary. They computed the total atmospheric deposition including an indirect loading term by assuming that 10% of the contaminant mass deposited to the watershed found its way into the estuary. Combined with estuary loading estimates from point source discharges, urban runoff and groundwater infiltration, their results indicated that total atmospheric deposition is a minor contributor of chlordane (1%), DDT (1%), dieldrin (1%), and endosulfan (0%) to the total annual loading of these pesticides to the bay. Due to the uncertainty in these estimates, ambient air sampling of 20 pesticides was conducted at the Gandy Bridge site from March to October 2001.

A list of the 20 pesticides, along with their respective ambient air detection limits, recovery rates, observation frequency and average concentration are presented in Table 6. Only seven of these 20 pesticides were detected, and by combining isomers, we reduced the seven to four pesticides—chlordane, DDE + DDT, endosulfan, and γ-HCH (lindane). Figure 14 illustrates the temporal variation of the ambient air concentration of these pesticides. Average atmospheric concentrations of chlordane, DDE, DDT, endosulfan and lindane are all below 10 ng m$^{-3}$, the national ambient air guideline for carcinogens (ATSDR, 2002).

In the US, the uses of DDT and chlordane have been banned since 1973 and 1988, respectively. DDT is no longer manufactured in the US, but one Tennessee-based company manufactures chlordane for export. DDE is both a contaminant of technical grade DDT, and a biodegradation product of DDT. DDT is currently manufactured in Mexico, and may also be a contaminant of another pesticide, difocol (ATSDR, 2002). Lindane and endosulfan, with restrictions, are still applied to crops and trees in the US, and both pesticides are imported and formulated in the US (ATSDR, 2002). Endosulfan and lindane have shorter environmental residence times than do

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### Table 6. Average daily ambient air PCB concentrations measured at the Gandy Bridge monitoring site from March 2001 to October 2001. The detection limit expressed as an ambient air concentration is based on a 324 m$^{-3}$ sampling air volume (n=36).

<table>
<thead>
<tr>
<th>PCB Congener</th>
<th>Detection Limit (ng m$^{-3}$)</th>
<th>Concentration (ng m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB-101</td>
<td>0.015</td>
<td>None detected</td>
</tr>
<tr>
<td>PCB-105</td>
<td>0.012</td>
<td>None detected</td>
</tr>
<tr>
<td>PCB-118</td>
<td>0.012</td>
<td>None detected</td>
</tr>
<tr>
<td>PCB-128</td>
<td>0.012</td>
<td>None detected</td>
</tr>
<tr>
<td>PCB-138</td>
<td>0.009</td>
<td>None detected</td>
</tr>
<tr>
<td>PCB-153</td>
<td>0.009</td>
<td>None detected</td>
</tr>
<tr>
<td>PCB-170</td>
<td>0.012</td>
<td>None detected</td>
</tr>
<tr>
<td>PCB-18</td>
<td>0.012</td>
<td>None detected</td>
</tr>
<tr>
<td>PCB-180</td>
<td>0.015</td>
<td>None detected</td>
</tr>
<tr>
<td>PCB-187</td>
<td>0.009</td>
<td>None detected</td>
</tr>
<tr>
<td>PCB-195</td>
<td>0.006</td>
<td>None detected</td>
</tr>
<tr>
<td>PCB-206</td>
<td>0.009</td>
<td>None detected</td>
</tr>
<tr>
<td>PCB-28</td>
<td>0.012</td>
<td>None detected</td>
</tr>
<tr>
<td>PCB-44</td>
<td>0.009</td>
<td>None detected</td>
</tr>
<tr>
<td>PCB-52</td>
<td>0.009</td>
<td>None detected</td>
</tr>
<tr>
<td>PCB-66</td>
<td>0.015</td>
<td>None detected</td>
</tr>
<tr>
<td>PCB-8</td>
<td>0.009</td>
<td>None detected</td>
</tr>
</tbody>
</table>
chlordane and DDT, with half-lives for water, soil and sediments reported in days instead of years. Endosulfan is not considered a carcinogen, but even at low water concentrations seems to disrupt the reproductive cycle of amphibians (Park, D., et al., 2001). The USEPA recommended Water Quality Criteria for protection of aquatic life in seawater is 0.034 µg L⁻¹ for endosulfan and 0.16 µg L⁻¹ for lindane (ATSDR, 2002).

**Table 6.** Average daily ambient air pesticide concentrations measured at the Gandy Bridge monitoring site from March 2001 to October 2001

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>LDL a (ng m⁻³)</th>
<th>Recovery (%)</th>
<th>Precision (RPD) b</th>
<th>Detection Frequency c (n = 39)</th>
<th>Average Concentration (ng m⁻³) d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrin</td>
<td>0.012</td>
<td>70-130</td>
<td>0-30</td>
<td>0</td>
<td>None detected</td>
</tr>
<tr>
<td>α-BHC</td>
<td>0.012</td>
<td>50-130</td>
<td>10-30</td>
<td>0</td>
<td>None detected</td>
</tr>
<tr>
<td>β-BHC</td>
<td>0.018</td>
<td>70-130</td>
<td>0-20</td>
<td>0</td>
<td>None detected</td>
</tr>
<tr>
<td>δ-BHC</td>
<td>0.012</td>
<td>30-90</td>
<td>0-10</td>
<td>0</td>
<td>None detected</td>
</tr>
<tr>
<td>γ-BHC (Lindane)</td>
<td>0.012</td>
<td>60-120</td>
<td>0-30</td>
<td>14</td>
<td>0.019</td>
</tr>
<tr>
<td>α-Chlordane</td>
<td>0.009</td>
<td>80-130</td>
<td>0-30</td>
<td>31</td>
<td>0.064</td>
</tr>
<tr>
<td>γ-Chlordane</td>
<td>0.012</td>
<td>80-130</td>
<td>0-30</td>
<td>34</td>
<td>0.083</td>
</tr>
<tr>
<td>DDD-p,p'</td>
<td>0.025</td>
<td>80-130</td>
<td>0-30</td>
<td>0</td>
<td>None detected</td>
</tr>
<tr>
<td>DDE-p,p'</td>
<td>0.018</td>
<td>70-130</td>
<td>0-30</td>
<td>7</td>
<td>0.015</td>
</tr>
<tr>
<td>DDT-p,p'</td>
<td>0.030</td>
<td>90-250</td>
<td>0-30</td>
<td>3</td>
<td>0.017</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>0.009</td>
<td>60-130</td>
<td>0-30</td>
<td>0</td>
<td>None detected</td>
</tr>
<tr>
<td>Endosulfan I</td>
<td>0.015</td>
<td>80-120</td>
<td>0-20</td>
<td>28</td>
<td>0.26</td>
</tr>
<tr>
<td>Endosulfan II</td>
<td>0.018</td>
<td>80-130</td>
<td>0-30</td>
<td>7</td>
<td>0.041</td>
</tr>
<tr>
<td>Endosulfan Sulfate</td>
<td>0.037</td>
<td>60-120</td>
<td>0-30</td>
<td>0</td>
<td>None detected</td>
</tr>
<tr>
<td>Endrin</td>
<td>0.025</td>
<td>100-140</td>
<td>0-30</td>
<td>0</td>
<td>None detected</td>
</tr>
<tr>
<td>Endrin Aldehyde</td>
<td>0.015</td>
<td>20-110</td>
<td>0-100</td>
<td>0</td>
<td>None detected</td>
</tr>
<tr>
<td>Endrin Ketone</td>
<td>0.015</td>
<td>80-170</td>
<td>0-30</td>
<td>0</td>
<td>None detected</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>0.012</td>
<td>70-130</td>
<td>0-30</td>
<td>0</td>
<td>None detected</td>
</tr>
<tr>
<td>Heptachlor Epoxide</td>
<td>0.009</td>
<td>60-120</td>
<td>0-20</td>
<td>0</td>
<td>None detected</td>
</tr>
<tr>
<td>Methoxychlor</td>
<td>0.035</td>
<td>80-180</td>
<td>0-20</td>
<td>0</td>
<td>None detected</td>
</tr>
</tbody>
</table>

a Lower detection level, expressed as an ambient air concentration is based on a 324 m⁻³ sampling air volume.

b Relative percent difference (RPD) between a fortified blank and a matrix spike.

c Counted were any concentrations above the lower detection level, including estimated and presumptive concentrations.

d One-half of the detection level concentration was used in calculating the average concentration for compounds with one or more concentrations above the detection limit.
Figure 14. Daily pesticide concentrations observed on a 1-in-6 day sampling schedule from March-October 2001 at the Gandy Bridge site in Tampa, Florida.

Only two pesticides—chlordane and endosulfan—were present in more than 50% of the samples, and it is for these pesticides that atmospheric deposition rates are calculated as described in Appendix A. Rainfall concentrations of pesticides were not measured, but the wet flux was estimated from the ambient air concentrations and total rainfall, based on gas/water partitioning (Appendix A, Equations 20 and 21). The direct deposition rates are given as totals in comparison with the Frithsen, et al. (1995) loading rates (Figure 12), and separately as wet and dry fluxes (Table 7).

The estimated deposition rates of chlordane to Tampa Bay were 4 µg m\(^{-2}\) yr\(^{-1}\) and 0.01 µg m\(^{-2}\) yr\(^{-1}\) for dry deposition of gas and particles, respectively; and 0.1 µg m\(^{-2}\) yr\(^{-1}\) and 0.3 µg m\(^{-2}\) yr\(^{-1}\) for wet deposition of gas and particles, respectively, assuming no flux of chlordane from the water to the air. Park, J., et al. (2001) reported for Galveston Bay atmospheric deposition fluxes of total chlordane as 0.52 µg m\(^{-2}\) yr\(^{-1}\) and 0.23 µg m\(^{-2}\) yr\(^{-1}\), for wet and dry (particulate only), respectively.
Modeled endosulfan deposition rates were 12 µg m\(^{-2}\) yr\(^{-1}\) and 0.02 µg m\(^{-2}\) yr\(^{-1}\) for dry deposition of gas and particles, respectively; 0.6 µg m\(^{-2}\) yr\(^{-1}\) and 0.7 µg m\(^{-2}\) yr\(^{-1}\) for wet deposition of gas and particles, respectively, assuming no flux of endosulfan from the water to the air.

Having narrowed the list of pesticides of concern to two, chlordane and endosulfan, we next summarize from literature ambient air concentrations for remote, rural and urban locales, where possible, with the intent to identify a concentration that represents a minimal anthropogenic impact.

![Figure 15](image)

**Figure 15.** A comparison of the 1995 (Frithsen et al., 1995) and 2001 direct atmospheric loading of pesticides to the Tampa Bay Estuary.

**Table 7.** Estimated total direct atmospheric loading (kg yr\(^{-1}\)) of chlordane and endosulfan to the Tampa Bay Estuary.

<table>
<thead>
<tr>
<th></th>
<th>Dry deposition</th>
<th>Wet Deposition</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gas</td>
<td>Particle</td>
<td>Gas</td>
</tr>
<tr>
<td>Chlordane</td>
<td>4</td>
<td>&lt;&lt;1</td>
<td>0.1</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>12</td>
<td>&lt;&lt;1</td>
<td>0.6</td>
</tr>
</tbody>
</table>

At a predominantly rural site in northern Alabama ambient air concentrations of α- and γ-chlordane averaged 0.047 and 0.025 ng m\(^{-3}\), respectively from January 1996 to May 1997.
Concentrations for these isomers in the air of Galveston Bay, Texas, averaged 0.030 and 0.039 ng m\(^{-3}\) between February 1995 and August 1996 (Park, J., et al., 2001). Integrated Atmospheric Deposition Network (IADN) Great Lake stations Brule River, Eagle Harbor, Sleeping Bear Dunes, Sturgeon Point and Chicago for 1996-1998 had average total chlordane concentrations of 0.009, 0.009, 0.016, 0.040 and 0.150 ng m\(^{-3}\) (Buehler, et al., 2001). The Brule River site is ~40 km from Duluth, Minnesota. According to Buehler, et al. (2001) the Brule Rivers site has higher PAH, but not PCB or pesticide, concentrations for winds from the direction of Duluth. Eagle Harbor, Sleeping Bear Dunes and Sturgeon Point are considered remote sites; however, Cortes, et al. (2000) saw elevated PAH concentrations at Sturgeon Point when the winds came from the direction of Buffalo, New York.

Background concentrations of total chlordane in arctic air for 1994 and 1995 were 0.0006-0.004 ng m\(^{-3}\) and 0.002-0.003 ng m\(^{-3}\), respectively (Kidd, et al., 1998). Average total chlordane concentrations recently measured in Tampa (Table 6) were higher than average concentrations observed in the arctic, rural Alabama, Galveston and the Great Lakes IADN stations with the exception of Chicago.

In Solomons, Maryland, rural ambient air concentrations of endosulfan I and II averaged 0.170 and 0.045 ng m\(^{-3}\), respectively from April-July 1995 (Harman-Fetcho, et al., 2000), and no endosulfan was found in rainfall. No endosulfan was found in rainfall in the Italian city of Rieti, where samples were collected from the urban core, a suburban settlement and an industrial park (Gidotti, et al., 2000). In a rural Canadian region where the pesticide was applied, the atmospheric level of endosulfan averaged 3.7 ng m\(^{-3}\) (ATSDR, 2002). The average endosulfan concentration at the Gandy Bridge site in Tampa was similar to that observed in rural Maryland.

The literature review offers evidence that the ambient air concentrations of chlordane and endosulfan are higher than “background” concentrations. Analysis of the ambient air concentrations and meteorology provides clues to the source of the pesticides.

For example, chlordane concentrations diminished with increasing wind speed, as shown in Figure 16, indicating dilution of atmospheric chlordane and not re-suspension of chlordane-bearing soils. The exponential shape of the chlordane versus wind speed relationship also suggests an interaction between wind speed and temperature, as atmospheric concentrations of chlordane decrease exponentially with temperature (Figure 17). Endosulfan concentrations were not correlated with wind speed (Figure 16).

Chlordane can evaporate from soils, structures or water to the air, and the evaporation rate is temperature-dependent (Harner, et al., 2001). The exponential relationship between atmospheric chlordane and temperature was significant, as can be seen in a Clausius-Clapeyron plot, Figure 17. Ambient air chlordane concentrations that are either strongly source influenced or transported from some distant will be less dependent on local temperatures and have a “flatter” slope than would be predicted from the vapor pressure heat of vaporization. For chlordane, the actual slope was –10,000, which is close to a theoretical slope of -9900 based on vapor pressure (Jantunen, et al., 2000). The exponential relationship between atmospheric endosulfan and temperature was not significant (Figure 17).
Another approach to discern between local and transported pesticide is to examine the isomer ratios. The $\gamma$ to $\alpha$ ratio is 1.2 for technical chlordane and 1.6 for vapors from soil-bound chlordane, which is a consequence of a higher $\gamma$-chlordane vapor pressure (Jantunen, 2000). Once in the atmosphere, $\gamma$-chlordane is photochemically degraded faster than $\alpha$-chlordane. Thus, for transported chlordane, the ratio can drop as low as 0.5 (ATSDR, 2002). In Figure 18 are graphed the time-series $\gamma$ to $\alpha$ ratios. From these data we can infer that for most of the sampling days, the chlordane volatilized from local reservoirs.

Endosulfan I is more stable than endosulfan II, and endosulfan II can convert over time to endosulfan I. The ratio of endosulfan I to endosulfan II in the technical grade product is $7:3$ (2.3). As endosulfan II was only infrequently detected, we surmise that the observed ratios are much greater than found in technical grade endosulfan. A plot of concentration versus time, Figure 14, has only a hint of seasonal dependence, with higher concentrations in the late spring and early fall. The lack of temperature or wind speed dependence, and the high endosulfan I to endosulfan II ratios, suggest that this pesticide was transported into the area, perhaps during seasonal applications throughout Florida. Dependence of endosulfan levels on wind direction was not strong enough to infer the direction of a source from the Gandy Bridge monitoring site.

Both chlordane and endosulfan ambient air concentrations had a weak positive correlation with rainfall, as is illustrated Figure 19. This suggests that rainfall facilitated volatilization of these pesticides from soil or other surfaces (Reichman, et al., 2000).

![Figure 16. Correlation of endosulfan ($r=0.15$) and chlordane ($r=-0.58$) with average daily wind speed. Wind speed was obtained for the Tampa International Airport from the National Climatic Data Center website. Chlordane and endosulfan concentrations were measured at the Gandy Bridge site in Tampa, Florida, from March-October, 2001. For chlordane, an exponential model fit the data better than a linear model, but neither model fit the endosulfan data.](image-url)
Figure 17. Clausius-Clapeyron plots for endosulfan \((r=-0.02)\) and chlordane \((r=-0.59)\). Average daily temperatures were obtained for the Tampa International Airport from the National Climatic Data Center website. Chlordane and endosulfan concentrations were measured at the Gandy Bridge site in Tampa, Florida, from March-October, 2001.

Figure 18. Ratio of \(\gamma\)- to \(\alpha\)-chlordane. Lower ratios imply more photodegradation of the \(\gamma\) isomer, and thus a longer transport distance.
Figure 19. Total daily rainfall was obtained for the Tampa International Airport from the National Climatic Data Center website. Pesticide concentrations were measured at the Gandy Bridge site in Tampa, Florida, from March-October, 2001.

3.3 Polycyclic Aromatic Hydrocarbons (PAHs)

Sediment concentrations of PAHs are high enough in some segments of Tampa Bay to pose an environmental health threat (McConnell, et al., 1996), but loading rates from point sources, urban runoff, and agricultural runoff to Tampa Bay have not yet been estimated. PAHs are found in nature, but are also formed by the incomplete combustion of fossil fuels. Fossil fuel combustion occurs in virtually every endeavor: transportation, power production, manufacturing, agriculture and recreation, as examples. For some watersheds, atmospheric deposition represents a significant input to the total surface water PAH burden, independent of adjacent land use. Across the nation increases in surface water sediment concentrations track increases in “vehicle miles traveled” (Van Metre, 2000). Recently, Dickhut et al. (2000) and Golomb et al. (2001) identified gasoline and diesel vehicles as the major contributors in the atmospheric deposition of PAHs to Chesapeake Bay, and Massachusetts Bay and Casco Bay, respectively.

A list of the 16 PAHs, along with their respective ambient air detection limits, recovery rates, observation frequency and average concentration are presented in Table 8. Six of these 16 PAHs were detected only once or not at all. Average atmospheric concentrations of individual PAHs were below 10 ng m\(^{-3}\), the national ambient air guideline for carcinogens (ATSDR, 2002).
Table 8. Average daily ambient polycyclic aromatic hydrocarbon (PAH) concentrations measured at the Gandy Bridge monitoring site from March to October, 2001

<table>
<thead>
<tr>
<th>PAH Compound</th>
<th>LDL(^a) (ng m(^{-3}))</th>
<th>Recovery (%)</th>
<th>Precision (RPD)(^b)</th>
<th>Detection Frequency(^c) (n = 36)</th>
<th>Average Concentration(^d) (ng m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acenanthene</td>
<td>0.37</td>
<td>50-110</td>
<td>0-30</td>
<td>1</td>
<td>0.19</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>0.37</td>
<td>50-110</td>
<td>0-30</td>
<td>0</td>
<td>None detected</td>
</tr>
<tr>
<td>Anthracene</td>
<td>0.25</td>
<td>70-130</td>
<td>0-30</td>
<td>24</td>
<td>0.32</td>
</tr>
<tr>
<td>Benz(a)anthracene</td>
<td>0.15</td>
<td>90-150</td>
<td>0-20</td>
<td>1</td>
<td>0.08</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>0.12</td>
<td>70-130</td>
<td>0-20</td>
<td>9</td>
<td>0.11</td>
</tr>
<tr>
<td>Benzo(b)fluoranthene</td>
<td>0.19</td>
<td>70-130</td>
<td>0-30</td>
<td>15</td>
<td>0.24</td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>0.15</td>
<td>70-140</td>
<td>0-30</td>
<td>1</td>
<td>0.08</td>
</tr>
<tr>
<td>Benzo(g,h,i)perylene</td>
<td>0.12</td>
<td>70-150</td>
<td>0-30</td>
<td>10</td>
<td>0.09</td>
</tr>
<tr>
<td>Chrysene</td>
<td>0.15</td>
<td>70-120</td>
<td>0-30</td>
<td>15</td>
<td>0.15</td>
</tr>
<tr>
<td>Dibenz(a,h)anthracene</td>
<td>0.22</td>
<td>70-140</td>
<td>0-20</td>
<td>0</td>
<td>None detected</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>0.22</td>
<td>80-150</td>
<td>0-20</td>
<td>35</td>
<td>3.3</td>
</tr>
<tr>
<td>Fluorene</td>
<td>0.10</td>
<td>60-120</td>
<td>0-30</td>
<td>34</td>
<td>0.87</td>
</tr>
<tr>
<td>Indeno(1,2,3-cd)pyrene</td>
<td>0.22</td>
<td>80-130</td>
<td>0-30</td>
<td>0</td>
<td>None detected</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.52</td>
<td>50-120</td>
<td>0-40</td>
<td>21</td>
<td>0.66</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.25</td>
<td>70-130</td>
<td>0-20</td>
<td>36</td>
<td>6.9</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.22</td>
<td>80-140</td>
<td>0-30</td>
<td>34</td>
<td>1.7</td>
</tr>
</tbody>
</table>

\(^a\)Lower detection level, expressed as an ambient air concentration is based on a 324 m\(^{-3}\) sampling air volume.

\(^b\)Relative percent difference (RPD) between a fortified blank and a matrix spike.

\(^c\)Counted were any concentrations above the lower detection level, including estimated and presumptive concentrations.

\(^d\)One-half of the detection level concentration was used in calculating the average concentration for compounds with one or more concentrations above the detection limit.

Figures 20 and 21 show the daily ambient air total and individual PAH concentrations, respectively. Concentrations were lower for the more volatile PAHs of naphthalene, fluorene and anthracene; and this may be more symptomatic of sampling bias (i.e., the loss of the PAH due to volatilization during sampling) than of an environmental trend. Comparisons of PAH concentrations for background urban sites are given in Table 9. The arctic and the Chicago PAH concentrations represent the extremes found in literature.

Total (\(\Sigma\)) PAH aerosol concentrations were 0.11, 0.20, and 0.22 ng m\(^{-3}\) for phenanthrene, fluoranthene and pyrene, respectively, collected predominantly in the fine particle fraction (<2 \(\mu\)m) during an August campaign at a site in northeastern Bavaria; concentrations for these PAHs were ~30 times higher in the winter than in the summer (Kaupp and McLachlan, 1999). In Miami, Lang, et al. (2001) collected an average of 2.4 ng m\(^{-3}\) of \(\Sigma\) PAH as total suspended particulate (TSP). At an urban site in Boston, Massachusetts, Allen, et al. (1996) observed aerosol concentrations of 1.3 ng m\(^{-3}\) for anthracene, 13.3 ng m\(^{-3}\) for phenanthrene, 14.8 ng m\(^{-3}\)
for fluoranthene, 8.1 ng m\(^{-3}\) for pyrene, with \(~50\%\) of these aerosols found in the coarse mode (>2 µm). We assumed that the individual PAH was in equilibrium with its condensed phase, which was modeled as an 0.5 µm aerosol (Appendix A). Rainfall concentrations of PAHs were not measured, but the wet flux was estimated from the ambient air concentrations and total rainfall, based on gas/water partitioning (Appendix A, Equations 20 and 21).

Figure 20. Daily total PAH concentrations observed on a 1-in-6 day sampling schedule from March-October, 2001 at the Gandy Bridge site in Tampa, Florida.

Table 9. Comparison of average PAH (gas + aerosol) concentrations measured at the Gandy Bridge site in Tampa, Florida, with PAH concentrations at “background” and urban sites. Concentrations are in ng m\(^{-3}\).

<table>
<thead>
<tr>
<th></th>
<th>Tampa Bay</th>
<th>Arctic(^a)</th>
<th>Birmingham, UK(^b)</th>
<th>Chicago(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Napthalene</td>
<td>0.66</td>
<td>Not reported</td>
<td>1.9</td>
<td>Not reported</td>
</tr>
<tr>
<td>Fluorene</td>
<td>0.87</td>
<td>0.01-0.05</td>
<td>7.0</td>
<td>75</td>
</tr>
<tr>
<td>Anthracene</td>
<td>0.32</td>
<td>0.001-0.007</td>
<td>0.61</td>
<td>14</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>6.9</td>
<td>0.002-0.01</td>
<td>3.8</td>
<td>200</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>3.3</td>
<td>0.009-0.02</td>
<td>2.1</td>
<td>44</td>
</tr>
<tr>
<td>Pyrene</td>
<td>1.7</td>
<td>0.007-0.02</td>
<td>3.3</td>
<td>25</td>
</tr>
<tr>
<td>ΣPAH</td>
<td>14</td>
<td>0.04-0.2</td>
<td>Not reported</td>
<td>430</td>
</tr>
</tbody>
</table>

\(^a\) Halsall, et al. (1997) in a 1993/1994 campaign at three arctic sites: Alert (Ellesmere Island, Canada), Tagish (western Yukon, Canada) and Dunai Island (eastern Siberia, Russia). Presented are the ranges for each compound of the arithmetic mean summertime (May-September) concentrations; reported wintertime concentrations were more than an order of magnitude higher.

\(^b\) Harrison, et al. (1996). Mean PAH concentrations measured at an urban site during a summertime campaign, in Birmingham, UK, which is a metropolitan area of ~2.5 million people.

\(^c\) Odabasi, et al. (1999) in a June-October, 1995 campaign on a building top in south Chicago.
Figure 21. Daily PAH concentrations observed on a 1-in-6 day sampling schedule from March-October 2001 at the Gandy Bridge site in Tampa, Florida.

The estimated total PAH deposition fluxes for Tampa Bay were $\sim 750 \, \mu g \, m^{-2} \, yr^{-1}$ for dry deposition of gas and particles, respectively; and $\sim 40 \, \mu g \, m^{-2} \, yr^{-1}$ for wet deposition of gas and particles, respectively, assuming no flux of PAH from the water to the air (Table 10). Comparisons for each PAH are shown in Table 11 for sites in the Chesapeake Bay region.
Golomb, et al. (2001), from November 1998 through May 2000 made direct wet and dry deposition measurements of PAHs at peninsular sites on Massachusetts Bay, Massachusetts, and Casco Bay, Maine. They estimated mean total PAH deposition fluxes of 830 µg m\(^{-2}\) yr\(^{-1}\) (dry) and 77 µg m\(^{-2}\) yr\(^{-1}\) (wet)* for the Massachusetts Bay site, which is near an urban center, and 81 µg m\(^{-2}\) yr\(^{-1}\) (dry) and 89 µg m\(^{-2}\) yr\(^{-1}\) (wet) for the more isolated Casco Bay site. Tampa Bay deposition rates are bracketed by deposition rates at both rural and urban sites on the US eastern seaboard.

**Table 10.** Estimated total direct atmospheric loading (kg yr\(^{-1}\)) of PAHs to the Tampa Bay Estuary

<table>
<thead>
<tr>
<th></th>
<th>Dry Deposition</th>
<th>Wet Deposition</th>
<th>Total Deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gas</td>
<td>Particle</td>
<td>Gas</td>
</tr>
<tr>
<td>Napthalene</td>
<td>7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fluorene</td>
<td>17</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Anthracene</td>
<td>30</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>385</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>229</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>Pyrene</td>
<td>105</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>ΣPAH</td>
<td>773</td>
<td>2</td>
<td>11</td>
</tr>
</tbody>
</table>

**Table 11.** Comparisons of net annual gas fluxes for Tampa Bay and Chesapeake Bay monitoring sites (Gustafson and Dickhut, 1997)*

<table>
<thead>
<tr>
<th></th>
<th>Tampa Bay (Urban)</th>
<th>Wolftrap (Rural)</th>
<th>York River (Semi-Urban)</th>
<th>Elizabeth River (Industrial)</th>
<th>Hampton (Urban)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Napthalene</td>
<td>-7</td>
<td>+1200</td>
<td>+820</td>
<td>+1100</td>
<td>+1300</td>
</tr>
<tr>
<td>Fluorene</td>
<td>-17</td>
<td>+81</td>
<td>-140</td>
<td>-64</td>
<td>-290</td>
</tr>
<tr>
<td>Anthracene</td>
<td>-30</td>
<td>--</td>
<td>-25</td>
<td>+4.8</td>
<td>-76</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>-385</td>
<td>-29</td>
<td>-740</td>
<td>-480</td>
<td>-1700</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>-229</td>
<td>-22</td>
<td>-170</td>
<td>+300</td>
<td>-250</td>
</tr>
<tr>
<td>Pyrene</td>
<td>-105</td>
<td>-25</td>
<td>-73</td>
<td>+29</td>
<td>-120</td>
</tr>
</tbody>
</table>

*Units are µg m\(^{-2}\) yr\(^{-1}\); multiply by 10\(^{-5}\) to convert to kg ha\(^{-1}\) yr\(^{-1}\). A net flux from the water to the air is (+), and from the air to the water (-). Fluxes for Tampa Bay are calculated assuming the water PAH concentrations are zero.

According to Dickhut, et al. (2000), motor vehicles and coal combustion accounted for 53% and 47%, respectively, of the PAHs that deposited to the surface of the Chesapeake Bay. In Chicago, the atmospheric apportionment of PAHs was 48% coal combustion, 26% natural gas, 14% coke ovens (steel production), and 9% vehicle emissions (Simcik, et al., 1999). Too few data for the higher molecular weight species, and apparent biases in the naphthalene and anthracene concentrations hampered our efforts to assign PAHs to source categories. For the few days of concurrent benzo(a)pyrene and benzo(g,h,i)perlene concentrations, the ratios of 1.0 to 2.5

* To make a direct comparison possible, their wet deposition fluxes reported per cm of rainfall were computed for a more typical Tampa Bay rainfall of 1070 mm.
pointed to coal- or oil-fired combustion; as does the prevalence (Table 8) and association (Table 12) of anthracene, phenanthrene, fluoranthene, and pyrene (Simcik, et al., 1999).

Correlations between the measured PAHs are presented in Table 12. Disproportionate photolysis and oxidation could explain the lack of stronger correlations between PAHs. Dimashki, et al. (2001) have developed reactivity ratios to explain the relative differences in PAH atmospheric decay rates from all removal pathways in an urban environment: from the most to the least reactive, anthracene > fluoranthene > phenanthrene > fluorene (no ratio given for pyrene).

**Table 12.** Correlations between PAHs.

<table>
<thead>
<tr>
<th></th>
<th>Naphthalene</th>
<th>Fluorene</th>
<th>Anthracene</th>
<th>Phenanthrene</th>
<th>Fluoranthene</th>
<th>Pyrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorene</td>
<td>0.55</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracene</td>
<td>0.07</td>
<td>0.12</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.41</td>
<td>0.48</td>
<td>0.70</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>0.77</td>
<td>0.32</td>
<td>0.51</td>
<td>0.66</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.49</td>
<td>0.16</td>
<td>0.64</td>
<td>0.60</td>
<td>0.90</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Concentrations of the most prevalent PAHs showed a negative correlation with wind speed, indicating dilution of the atmospheric PAHs and not re-suspension of PAH-bearing soils (Figure 22). Moreover, these PAHs had no significant correlation with ambient air coarse particulate matter concentrations but had positive associations with fine particulate matter (particles 2.5 µm and smaller or PM$_{2.5}$) concentrations (Figure 23). PM$_{2.5}$ consists of soot, smoke, condensed gases (for example, sulfuric acid), metal salts and oxides, and atmospherically formed aerosols such as ammonium sulfate. Fine particles are most typically derived from anthropogenic combustion of fossil fuels, but fine particle soils, forest fires and volcanic emissions also contribute to PM$_{2.5}$ concentrations (Seinfeld and Pandis, 1998). The increase in ambient air PAH concentrations for lower wind speeds and higher PM$_{2.5}$ concentrations is evidence that the PAHs are generated or evaporated locally and accumulate in the urban atmosphere on days with calm winds.
**Figure 22.** Dependence of ambient air fluoranthene \( (r = 0.53) \), fluorene \( (r = 0.27) \), pyrene \( (r = 0.52) \) and phenanthrene \( (r = 0.40) \) concentrations on average daily wind speed.

**Figure 23.** Dependence of ambient air fluoranthene \( (r = 0.33) \), fluorene \( (r = 0.51) \), pyrene \( (r = 0.23) \) and phenanthrene \( (r = 0.49) \) concentrations on average daily PM\(_{2.5}\) (PMFine) concentration.

**Figure 24.** Clausius-Clapeyron plots for fluoranthene and pyrene. Average daily temperatures were obtained for the Tampa International Airport from the National Climatic Data Center website. Fluoranthene and pyrene concentrations were measured at the Gandy Bridge site in Tampa, Florida, from March-October 2001.

Only fluoranthene and pyrene exhibited a significant exponential relationship with temperature (Figure 24). Based on the slope of the regressions in Figure 24, both had reaction enthalpies of \( \sim 62 \text{ kJ mol}^{-1} \), close to the reaction enthalpy for vaporization and a factor of \( \sim 2 \) higher that the reaction enthalpies seen at the IADN sites on the Great Lakes (Cortes, et al., 2000). From the high correlation \((r=0.90)\) between fluoranthene and pyrene, we can safely surmise that these two atmospheric constituents came from the same source or source category, and one candidate
among many is the volatilization of these compounds from the bay.

Unlike the pesticides chlordane and endosulfan, the PAH concentrations for fluoranthene, fluorene, pyrene and phenanthrene were lower when rainfall was higher, as illustrated in Figure 25 for phenanthrene. This negative correlation would be expected if these PAHs were in the atmosphere predominantly as fine particles, which are efficiently scavenged from the atmosphere during a rainfall (Poster and Baker, 1996).

**Figure 25.** Total daily rainfall was obtained for the Tampa International Airport from the National Climatic Data Center website. Ambient air phenanthrene concentrations were measured at the Gandy Bridge site in Tampa, Florida, from March to October 2001.

A linear regression analysis of PAHs and sulfur dioxide, nitrogen oxide, nitrogen dioxide and NOx (nitrogen oxide plus nitrogen dioxide) revealed no strong trends between emissions of these primary pollutants and PAH concentrations in the atmosphere, with the one exception of a markedly positive correlation of fluorene with nitrogen dioxide (NO₂), as graphed in Figure 26. The lack of a corresponding correlation of fluorene with sulfur dioxide hints that its source may be motor vehicles or gas-fired turbines and not coal- or oil-fired combustion.
Figure 26. Ambient air phenanthrene ($r = 0.24$) and fluorene ($r = 0.4$) versus nitrogen dioxide (NO$_2$) concentration for measurements made at the Gandy Bridge site in Tampa, Florida, from March to October 2001.

From our correlation and regression analyses we have inferred that the PAHs are likely emitted or volatilized in the gas phase from local sources but are present in the atmosphere as fine particles; fluoranthene and pyrene have a strong dependence on ambient temperature that points to volatilization either from land or water, while fluorene could be emitted from motor vehicles or gas-fired turbines.

For the Tampa Bay area, an intensive PAH measurement period would have tremendous value in quickly resolving extant questions about the PAH particle-bound fraction, wet deposition rates and air-water exchange of gases. If timed to coincide with the Bay Regional Atmospheric Chemistry Experiment (BRACE), PAH measurements would also support source apportionment of local and transported ambient air pollution among the utility, industrial, and transportation source categories. Combined with BRACE-derived concentration and deposition estimates for metals and volatile organic compounds, an improved estimate of the ambient air and water PAH concentrations, the direction and magnitude of the PAH fluxes, and the apportionment of these air toxins between the source categories would provide enough scientific data to assess the human and environmental health benefit of planned or proposed source strength reductions. Such an assessment would serve as input to state, regional or local urban development policy-making, and nationally as a model for other estuary programs. This follow-on effort has been funded by the USEPA through the TBEP.
3.4 Metals

Persistent, bioaccumulative or toxic metals present in the sediments of the Tampa Bay Estuary at concentrations that may pose a risk to aquatic species include arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver and zinc (Frithsen, et al., 1995; McConnell, et al., 1996). Frithsen, et al. (1995) used the geometric mean of Florida rainfall concentration data reported in literature to estimate the direct deposition of these metals from the atmosphere to the Tampa Bay Estuary. They computed the total atmospheric deposition including an indirect loading term by assuming that 10% of the contaminant mass deposited to the watershed found its way into the estuary. Combined with estuary loading estimates from point source discharges, urban runoff and groundwater infiltration, their results indicated that total atmospheric deposition is a significant contributor of cadmium (46%), chromium (13%), copper (18%), iron (11%), and lead (12%), and a minor contributor of arsenic (7%), zinc (4%) and mercury (1%) to the total annual loading of these metals to the bay.

To improve the direct atmospheric loading estimate, both wet and dry deposition rates for these metals were calculated from ambient air and rainfall concentrations measured at the Gandy Bridge site from January 2000 to March 2001. A comparison of the 1995 (Frithsen, et al., 1995) and 2000 direct loading rates to the Tampa Bay estuary of arsenic, cadmium, chromium, iron, mercury, nickel, copper, lead, silver, and zinc are presented in Figure 27. For arsenic, cadmium, chromium, nickel and lead, the 2000 direct atmospheric loading rates were well below the 1995 estimates; however, the loading rates for copper, mercury, zinc and iron were significantly above the previous estimates.

We recalculated the direct plus indirect atmospheric deposition portion of the 1995 loading rates to reflect the revised 2000 loading rates, and arsenic, chromium, lead and mercury contributions dropped to less than 5%; cadmium and zinc to ~10%, copper to ~20%, and iron to ~40% of the total loading from all point and non-point sources. No total loading rates were available for nickel and silver. An explanation of the sampling and laboratory analyses, and the approach for calculating the deposition rates can be found in Appendix A.

Landing, et al. (1995) as part of the 1993-1994 Florida Atmospheric Mercury Study measured at five sites south Florida sites both bulk and rainfall concentrations of trace metals and mercury. They found bulk atmospheric deposition rates of 86-141 µg m⁻² yr⁻¹ for arsenic; 16-106 µg m⁻² yr⁻¹ for cadmium, 430-1,840 µg m⁻² yr⁻¹ for copper; 32,000-104,000 µg m⁻² yr⁻¹ for iron; 403-974 µg m⁻² yr⁻¹ for lead; 15-28 µg m⁻² yr⁻¹ for mercury; 1,700-4,130 for nickel; and 5,320-11,920 µg m⁻² yr⁻¹ for zinc. With the exception of a higher deposition rate for nickel, the FAMS trace metal deposition rates are reasonably consistent with atmospheric deposition rates reported for Tampa Bay.

Over the last decade, emissions controls on motor vehicles, incinerators, industries, and power plants have no doubt played a definitive role in lowering the atmospheric deposition of toxic metals. For example, from 1987-1996, ambient air concentrations of lead dropped by 75% with the removal of tetraethyl lead from gasoline (USEPA, 1998). Population growth, the growth of
vehicle miles traveled and a larger vehicles, and a strong economy through the 1990s have counteracted to some extent the expected improvements in urban air quality, and may explain in part the dichotomy of the trends shown in Figure 27.

Table 13 compares recent estimates of toxic metal wet and dry deposition to the coastal waters of the Gulf of Maine and Massachusetts Bay with those of Tampa Bay. For the Gulf of Maine, the dry deposition rates were similar to those for Tampa Bay of the listed metals except for higher rates for nickel and silver. Dry deposition rates of metals to Massachusetts Bay, however, were considerably above those for Tampa Bay.

Pike and Moran (2001) modeled for the Gulf of Maine an average deposition velocity of 0.3 cm s⁻¹, while Golomb, et al. (1997) applied separate deposition velocities of 0.025 cm s⁻¹ and 0.25 cm s⁻¹ to the fine and coarse particle concentrations, respectively, for Massachusetts Bay, to obtain dry deposition rates of trace metals. This may in part explain the large differences between the deposition rates reported for these two water bodies (Table 13).

Average annual deposition velocities for particles depositing to Tampa Bay were calculated for fine (0.5 µm) and coarse particles (5 µm) with a Williams-type model for one year of 30-minute meteorological data acquired at a station in the middle of the bay, and were 0.008 cm s⁻¹ and 0.08 cm s⁻¹, respectively. In general, the lower deposition velocities for Tampa Bay can be explained by the lower surface wind speeds over the bay, relative to the larger water bodies. The choices of fine and coarse particle sizes are consistent with scanning electron microscope photographs of particles collected at the Gandy Bridge site.

The annual wet deposition rates of copper and zinc to the Tampa Bay estuary were significantly higher than the wet deposition of these metals to either the Gulf of Maine or to Massachusetts Bay (Table 13).

Mason, et al. (1997) reported wet total mercury deposition to Chesapeake Bay in the range of 10-20 µg m⁻² yr⁻¹, with dry deposition rates ~10% of the wet deposition rates. For the Tampa Bay estuary these results agree with the 14 µg m⁻² yr⁻¹ wet deposition flux, but not the higher 8 µg m⁻² yr⁻¹ dry deposition flux (Table 13). From 1993-1996 the annual average wet deposition flux of mercury at a remote site in Barbados was 5 µg m⁻² yr⁻¹, compared with the 11 µg m⁻² yr⁻¹ in the Florida Keys and 19-23 µg m⁻² yr⁻¹ across southern Florida for the same time period (Guentzel, et al., 2001).

To some extent, the sources of the toxic metals that reach Tampa Bay can be deduced by their covariance in air and rainwater samples. For example, typical constituents of soil or road dust are silicon, aluminum, iron, potassium, manganese and titanium. These metals are also present in motor vehicle exhaust, however, the mass ratio of aluminum to manganese in soil or road dust is ~50-100, but ~1 in tailpipe exhaust (Chan, et al., 1999). The high correlation of these metals, and mass ratios consistent with soil particles as shown in Figure 28, provide strong evidence that the source of atmospheric iron and chromium that is deposited to Tampa Bay is suspended soil or road dust.

Iron can be transported across the Atlantic Ocean from the Sahara Desert at concentrations high
enough to produce a visible reddish haze in the Tampa Bay area (Prospero, 1999). Although iron is not considered a toxic metal, it may be a limiting nutrient in stimulating harmful algal blooms such as red tide (Walsh and Steidinger, 2001).

Elevated arsenic, copper, zinc, mercury, cadmium and lead concentrations identify the emissions from combustion, and more specifically, emissions from municipal waste incinerators, coal-fired power plants and motor vehicles. With the exception of mercury, the significant correlations of these metals (Figure 29) supply reasonable evidence that these combustion processes are the predominant sources of the atmospheric arsenic, copper, zinc and lead that are deposited to Tampa Bay.

Another source of copper in an urban setting is the frictional wear of vehicle brake pads. A recent report by Connick (2001) tallies ~1 kg of frictional material per vehicle of which ~5% is copper. Copper abraded from brake pads could reach the bay either from urban runoff or by atmospheric deposition of re-suspended road dust. Tires are a source of zinc attrition, and thus the tight correlation of copper and zinc could be road emissions as well as combustion.

The presence of copper at elevated concentrations in the sediments of Tampa Bay and its association with toxic sediments based on bioassays (McConnell, et al., 1996; Long and Greening, 1999), its prevalence in ambient air and rainwater and its relatively high direct deposition to Tampa Bay are a “red flag” for continued accumulation of this toxin in the estuary and perhaps the need to identify a critical loading threshold.

Nickel and vanadium have been strongly linked to crude oil burning (Chow, et al., 1992). Near Tampa Bay crude oil is burned not only at regional utility power plants and industrial plants, but also in the large tankers and cruise ships that access the ports of Tampa and Manatee. The significant covariance of these metals in air and rainwater samples (Figure 22) points to crude oil burning as a source of their atmospheric concentrations.

No strong correlation of mercury with other metals or inorganic ions gave conclusive evidence as its source of atmospheric concentrations over Tampa Bay. In a study conducted adjacent to the Everglades in Dade and Broward County, Dvonch, et al. (1998) hypothesized that local combustion sources, which included oil-fired utilities, municipal waste incinerators, medical waste incinerators, and cement kilns, were the largest contributors of mercury in the collected rainfall. Guentzel, et al. (2001), however, argued that during the summertime in southern Florida more than 50% of the mercury in rainfall may have been transported long-distances in the upper troposphere and carried to the surface in rainfall during deep convective thunderstorms.

A principal components analysis of the rainwater trace metals data yielded five significant factors, as shown in Table 14. The first factor (Prin1) explained ~44% of the covariance in the metals concentrations, and from the heavy weights on aluminum, chromium, iron, manganese, strontium and titanium is interpreted as geological material (soil) (Chan, et al., 1999). From the lesser but still positive weights on combustion species such as vanadium and nitrate, and sea salt elements like sodium and magnesium, this factor is better described as “urban dust.”

The second factor has strong positive weights for copper, cadmium and lead; and strong negative
weights for sodium, magnesium and chloride. The anti-weights of sea salt point to contributions from this source category when the air is stagnant. The third factor, has strong positive weights for copper, cadmium, arsenic, sodium and chloride, and strong negative weights for titanium, antimony and cesium, and suggest emissions that are mixed with marine air. These two factors probably represent “mixed combustion” from motor vehicles, municipal solid waste incinerators, and coal-fired power plants. The second and third factors explained ~14% and ~10% of the data covariance, respectively.

The fourth factor has strong positive weights on mercury, antimony, potassium, calcium and nitrate; strong negative weights on aluminum and nickel. This factor may indicate municipal waste incineration (Dvonch, et al., 1999), and explained ~9% of the data covariance.

The fifth factor, which explains ~6% of the data covariance, contains strong positive loadings on nickel and vanadium, which are distinct markers of oil combustion (Chow, et al., 1992).

The factors are consistent with the simple linear regressions already presented, but give clues to how all of the metals in rainwater might be apportioned across the source categories. Cheng, et al. (2000) give an example of a similar apportionment.
Figure 27. A comparison of the 1995 (Frithsen et al., 1995) and direct atmospheric loading of toxic metals to the Tampa Bay Estuary.
Table 13. Comparison of direct atmospheric deposition rates of metals to Tampa Bay, to the Gulf of Maine (Pike and Moran, 2001), and to Massachusetts Bay (Golomb, et al., 1997). Units are $\mu$g m$^{-2}$ yr$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>Tampa Bay</th>
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<th>Massachusetts Bay</th>
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<tr>
<td></td>
<td>Wet</td>
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<td>Wet</td>
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<td>Dry</td>
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<td>Chromium</td>
<td>180</td>
<td>25</td>
<td>78</td>
<td>41</td>
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<tr>
<td>Copper</td>
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<td>96</td>
<td>670</td>
<td>160</td>
<td>500</td>
<td>2000</td>
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<tr>
<td>Iron</td>
<td>24,000</td>
<td>8,300</td>
<td>14,000</td>
<td>11,000</td>
<td>36,000</td>
<td>110,000</td>
</tr>
<tr>
<td>Lead</td>
<td>530</td>
<td>80</td>
<td>780</td>
<td>370</td>
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<tr>
<td>Mercury</td>
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<td>36</td>
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<td>220</td>
<td>8,300</td>
<td>1,000</td>
<td>2,700</td>
<td>5,100</td>
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nr: not reported
Figure 28. Correlation of aluminum with silicon ($r=0.99$), iron ($r=0.98$), potassium ($r=0.94$), titanium ($r=0.99$), manganese ($r=0.97$), and chromium ($r=0.58$) in ambient air particles 10 µm in diameter or smaller (upper graph); correlation of aluminum with iron ($r=0.97$), manganese ($r=0.96$), titanium ($r=0.82$), and chromium ($r=0.86$) in rainwater (lower graph).
Figure 29. Correlation of copper with zinc ($r=0.75$) and lead ($r=0.65$) in ambient air particles 10 µm in diameter or smaller (upper graph); correlation of copper with zinc ($r=0.80$), lead ($r=0.83$), arsenic ($r=0.79$), and cadmium ($r=0.76$) in rainwater (lower graph).
**Figure 30.** Correlation of nickel with vanadium ($r=0.72$) in ambient air particles 10 µm in diameter or smaller (upper graph) and correlation of nickel with vanadium ($r=0.87$) in rainwater (lower graph).
Table 14. Principal components analysis for metals concentrations in rainwater using SAS® PRINCOMP procedure. Positive and negative weights less than 0.25 are shown in a lighter type to de-emphasize their relative importance.

<table>
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<th>Cumulative</th>
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<td>6.70872705</td>
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<tr>
<td>2</td>
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<td>3</td>
<td>2.18138157</td>
<td>0.26708881</td>
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</tr>
<tr>
<td>5</td>
<td>1.30736217</td>
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<table>
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<tr>
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<th>Prin3</th>
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<td>A127</td>
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<td>Ti47</td>
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<td>-.280774</td>
<td>-.114516</td>
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<tr>
<td>V51</td>
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<td>-.189020</td>
<td>0.523714</td>
</tr>
<tr>
<td>Cr52</td>
<td>0.255112</td>
<td>0.131519</td>
<td>-.019271</td>
<td>-.211859</td>
<td>-.137087</td>
</tr>
<tr>
<td>Mn55</td>
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<td>-.173085</td>
<td>-.183756</td>
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<td>Fe57</td>
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<td>0.015427</td>
<td>0.090365</td>
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<td>Cu63</td>
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<td>0.352167</td>
<td>0.256498</td>
<td>-.062411</td>
<td>0.183517</td>
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<tr>
<td>Sr88</td>
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<td>Cd111</td>
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<td>0.263828</td>
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<td>Sb</td>
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<td>0.058270</td>
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<td>Cs133</td>
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<td>-.395332</td>
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<td>Pb208</td>
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<td>Ca</td>
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<tr>
<td>Mg</td>
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<td>Cl</td>
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<td>0.337456</td>
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<td>-.358183</td>
</tr>
</tbody>
</table>
3.5 Summary and Recommendations

- The source of PCBs to the atmosphere is probably the bay itself, and the annual loading of total PCBs by direct atmospheric deposition to the Tampa Bay is likely less than 50% of the 1995 estimate of 11 kg. With respect to atmospheric PCBs, we recommend no further action on the part of the Tampa Bay Estuary Program.

- Of the pesticides monitored, only chlordane and endosulfan had detectable concentrations in more than 50% of the samples. The estimated direct deposition rate of chlordane from the atmosphere to Tampa Bay is low at ~4 kg yr\(^{-1}\), which is less than 50% of the 1995 estimate of 13 kg yr\(^{-1}\); moreover, the source of chlordane to the atmosphere is most likely the re-volatilization of chlordane from local soil and structure surfaces, a source which should diminish with time. The inferred sources of the chlordane, however, are relatively strong local reservoirs. Thus, urban and agricultural runoff of chlordane may still pose a threat to the health of the Bay and we recommend that the Tampa Bay Estuary Program continue its monitoring of chlordane in bay sediments.

- Endosulfan most likely has as its sources statewide application to fruit and vegetable crops. The atmospheric deposition rate to Tampa Bay was relatively low at ~13 kg yr\(^{-1}\). In the more rural southeastern coast of Tampa Bay, however, fruit and vegetable farming are still important and endosulfan use may have a more local impact on the estuary. We recommend that the Tampa Bay Estuary Program survey regional practices and policies regarding endosulfan application close to estuary to determine if further monitoring or modeling is necessary.

- The direct atmospheric deposition rates to Tampa Bay of arsenic, cadmium, chromium, nickel and lead were well below the 1995 estimates, however, the rates for copper, mercury, zinc and iron were significantly above the previous estimates. The apparent association of copper with regional combustion emissions suggests that future control measures may be successful in reducing the atmospheric flux of copper to Tampa Bay. Research already planned as part of the Bay Regional Atmospheric Chemistry Experiment (BRACE) may elucidate the more specific local emission sources of copper. We recommend in the interim, however, that the Tampa Bay Estuary Program propose to Tampa Bay stakeholders a regional inventory of point and non-point copper releases to both air and water, and the development of a copper critical loading threshold.

- Iron can be transported across the Atlantic Ocean from the Sahara Desert at concentrations high enough to produce a visible reddish haze in the Tampa Bay area and may be a requisite nutrient for harmful algal blooms such as red tide. The impact of these red tides on local (tourist) economies, on coastal ecology, and on human health are severe enough to merit pilot studies on the relationship between atmospheric iron and coastal blooms of harmful algae or bacteria.

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8 The estimate of the direction and magnitude of the net flux could be made if contemporary air, water and sediment concentration data were available for each bay segment.
Although the atmospheric deposition of mercury was projected by Frithsen et al. (1995) to be less than 5% of the 650 kg yr\textsuperscript{-1} total loading to Tampa Bay (and more specifically to Old Tampa Bay and Hillsborough Bay), the deposition rate may be high enough to warrant a National Trends Network Mercury Deposition Monitoring site. In conjunction with the BRACE, USEPA and University of Michigan researchers will characterize more completely the atmospheric concentrations of mercury and the sources of mercury emissions. The pending air pollution control measures and changes in utility source emissions should substantially reduce local emissions of mercury. With respect to mercury deposition, no additional actions are as yet recommended.
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APPENDIX A METHODS

Nitrogen

Wet deposition

Wet deposition sampling was done following the protocols developed by the National Atmospheric Deposition Program (NADP) Atmospheric Integrated Research Monitoring Network (NADP/AIRMoN). A wet bucket (Aerochemetrics, Inc.) collected daily rainfall samples, and samples of greater than 10 ml were sent to the Central Analytical Laboratory (CAL) of the Illinois State Water Survey, where the samples were analyzed by the same methods as those used by the NADP/AIRMoN program. Results are given for ammonium, chloride, sulfate, potassium, magnesium, specific conductance, orthophosphate, nitrate, sodium, calcium, and pH on rainfall samples. In addition to the rainfall samples, rainfall amounts are taken from an on-site rain gauge.

Wet deposition rates are a function of both the rainwater concentration of each analyte and the rainfall amount, as shown in Equation 1, where \( C_{\text{rain}} \) is the concentration of nitrogen in the rainfall (mg-N/L), \( D \) is the depth of rainfall (mm), 0.01 is a units conversion factor, and \( F_{\text{wet}} \) is the wet flux of nitrogen (kg-N/ha/day). \( F_{\text{wet}} \) was summed over each month and year to get the monthly and annual nitrogen wet deposition rates, respectively.

Equation 1. \[ F_{\text{wet}} = 0.01 \cdot C_{\text{rain}} \cdot D \]

Dry deposition

Dry deposition rates were calculated from the product of the ambient air concentration of the analyte \( C_{\text{air}} \) (µg/m³), the dry deposition velocity \( v_d \) (m/s), and the integration time \( t \) (days), as shown in Equation 2, where 0.864 is the appropriate units conversion factor for a dry deposition flux \( F_{\text{dry}} \) in kg-N/ha/month. \( F_{\text{dry}} \) was summed over the year to get the annual dry deposition rates.

Equation 2. \[ F_{\text{dry}} = 0.864 \cdot C_{\text{air}} \cdot v_d \cdot t \]

The ambient air concentrations of gaseous ammonia and nitric acid and particulate ammonium and nitrate were obtained from an annular denuder system (URG, Inc.). The annular denuder system (ADS) consisted of a 2.5-µm particle aerodynamic diameter cut-point PTFE-coated cyclone inlet, two 150-mm long gas denuders, and a filter pack in series. The first of two denuders was coated with sodium carbonate to absorb nitric acid and sulfur dioxide. The second denuder was coated with citric acid to trap ammonia. A single 47-mm diameter nylon filter collected particulate nitrate, sulfate and ammonium. The ADS was operated at a flow rate of 10 L/min for 24 hours every 6th day, coincident with the USEPA National Ambient Monitoring System schedule for particulate matter.
EPCHC technicians forwarded weekly the denuders and filter packs to Harding ESE, Inc. (Gainesville, FL), for analysis. ESE chemists extracted the denuders and filters in an aqueous solution and analyzed the extract for sulfate and nitrate by ion chromatography and for ammonium by automated colorimetry.

The NOAA buoy model and an integrated William’s model were employed to calculate the gas and particle deposition velocities, respectively (Valigura, 1995; Williams, 1982). Required inputs to these models were wind speed, air temperature, water temperature and relative humidity, wind measurement height, and particle diameter. A particle diameter of 0.5 µm was assumed for nitrate, sulfate and ammonium, consistent with observed fine particle modes for these compounds. Weather data from the mid-bay meteorological station were processed with surface weather observations from the Tampa International Airport and water temperature measurements from Clearwater Beach to obtain as complete a data set as possible of hourly over-water meteorology from August 1996 through July 2001.

**Bulk deposition**

From May 1999 to February 2000 at the Gandy Bridge site, the bulk nitrogen deposition samples were collected with a 12.2-cm diameter polycarbonate funnel attached to a 2-L polyethylene bottle via PTFE® tubing. The funnel and bottle combination was washed, rinsed, dried and covered with polyethylene bags prior to and following a one-week deployment, wrapped in aluminum foil and installed at a height of 2.5 m. The EPCHC environmental laboratory analyzed the funnel rinseate and bottle rainwater for ammonia (organic plus inorganic) by the Total Kjeldahl Nitrogen (TKN) method and nitrate by ion chromatography.

From October 2001-November 2001, the bulk deposition sampling was repeated with daily instead of weekly sample collection (Hendrix et al., 2002). In this latter study, the funnel was rinsed with 100 mL of sulfuric acid and split into two subsamples for analyses by TKN and ion chromatography (IC). Organic ammonia was calculated as the difference between TKN and IC ammonia. Samples were considered “clear” if no bugs, debris, bird droppings, feces, frogs or pollen were evident.

Bulk deposition rates were calculated from Equation 3, where \( C_N \) is the total nitrogen mass (mg-N), \( A \) is the area of the funnel opening (0.0113 m²), 0.01 is a units conversion factor, and \( F_{bulk} \) is the bulk nitrogen flux (kg-N/ha/day).

Equation 3. \[ F_{bulk} = 0.01 \cdot \frac{C_N}{A} \]

**Stable nitrogen isotopes**

Isotopic ratios of nitrogen in the atmosphere may indicate the origin or history of an air mass. The ratio \( \delta^{15}N \) for clean air is 0‰ and is computed from Equation 4, where \( R_{sa} \) is the isotopic ratio of the sample; \( R_{std} \) is the isotopic ratio of the standard, in this case clean air (i.e., \( N_2 \)); and \( \delta \) (‰) is the enrichment or depletion of the stable isotope relative to the standard.
Equation 4. \[ \delta = \left( \frac{R_{\text{m}}}{R_{\text{std}}} - 1 \right) \cdot 1000 \]

For nitrogen stable isotope (\(^{15}\text{N}\)) analyses, from July 1998 to October 1999 wet-only precipitation samples were collected in a pre-cleaned stainless steel bucket daily following a rainfall. At the time of collection the samples were transferred into a pre-cleaned glass bottles, which were capped with aluminum foil and lids, immediately frozen and shipped on dry ice to the University of Virginia for analysis (Earls, 2001).

Velinsky, et al. (1989), describes determination of the \(^{15}\text{N}\) composition of ammonium and nitrate. In brief, the method reduced nitrate to ammonium, and the ammonium was converted to ammonia by raising the pH of the sample aliquot, then re-trapped with acid and concentrated on a zeolite molecular sieve as ammonium. The zeolite containing the ammonium was combusted and through sequential catalytic reactions with cuprous oxide and copper was oxidized to nitrogen oxide then reduced to nitrogen gas (N\(_2\)). The nitrogen was separated at cryogenic temperatures from the accompanying combustion gases, concentrated on a molecular sieve, and analyzed with an isotope ratio mass spectrometer.

From February 1999 to November 1999, ambient air particulate samples were collected every six days for \(^{15}\text{N}\) analyses. Air samples were integrated for 24 hours and the sampling apparatus operated with a 2.5-\(\mu\)m cut-point at a flow rate of 10 L/min onto pre-combusted glass fiber filters. Upon collection, the samples were immediately frozen and shipped on dry ice to the University of Virginia for analysis (Earls, 2001).

Particulate nitrogen was detected by converting the particulate nitrogen present on the filter to nitrogen (N\(_2\)) through a combustion process in an elemental analyzer. The isotopic ratios of the nitrogen gas were then determined by mass spectrometry (Velinsky, et al., 1989).

**Passive sampling of ammonia**

To describe the ambient ammonia concentration gradient across urban and industrial Tampa, in October 2001 more than 90 passive sampling devices (PSDs) were simultaneously deployed for two weeks in an area bounded on the north by Interstates 4 and 275, including the locally famous “malfunction junction,” to the east by Interstate 75, to the south by the Gibsonton, and to the west by Tampa Bay. On the southern Tampa peninsula, PSDs were placed south to Bay-to-Bay Boulevard (Tate, 2002). Within the regional coverage were suburbs, an urban center, major highways, port activities, fertilizer manufacturing, wastewater treatment, coal-combustion power plants, warehousing and dairy farming. The ambient air ammonia concentrations were plotted with Surfer \(^{7}\)® and spatially interpolated by kriging (Tate, 2002).

**Metals**

Ambient air fine (<2.5 \(\mu\)m in diameter) and coarse (>2.5 \(\mu\)m and <10 \(\mu\)m in diameter) particle samples were obtained with a dichotomous sequential air sampler (Rupprecht & Patashnick, Inc., Model 2025 Partisol®-Plus), which has been operating on a daily schedule at the Gandy Bridge...
monitoring site since January 2000. Samples were collected for 24 hours on 47-mm PTFE® filters at a total flow rate of 16.7 L/min. Filters were pre- and post-weighed in Tallahassee at the Florida Department of Environmental Protection (FDEP) laboratory in accordance with 40CFR50 requirements. For more details on the storage, handling, data analyses and uncertainties for the particulate matter measurements, refer to Poor et al., 2002.

Forty-five filters plus laboratory and field blanks, one for every 6th day of the measurement period from January 2000 to September 2000, were selected for x-ray fluorescence (XRF) analyses at the EPA National Environmental Research Laboratory in Research Triangle Park, North Carolina. XRF spectrometry (Kevex) can quantify elements for atomic numbers 11-82 (sodium through lead) and was calibrated with NIST special reference materials. XRF results were corrected for blank background, attenuation and interferences.

From March 2000 to March 2001, a wet-only precipitation collector (MIC, Inc.) re-engineered to funnel rainfall into four separate bottles, captured rainfall at the Gandy Bridge site for the purpose of trace metal and mercury analyses. Pre-cleaned funnels and 1-L bottles were checked daily for rainfall. If present, rainfall was decanted into pre-cleaned 250 mL bottles, immediately chilled, and returned on ice to the University of Michigan Air Quality Laboratory for analyses. After either a rainfall or one week with no rainfall, funnels and bottles were also returned to the University of Michigan for re-cleaning. A more detailed description of the modified MIC collector, the funnel and bottle design and materials, the pre- and post-cleaning and handling procedures can be found in Landis and Keeler (1997).

Trace metal analyses were by inductively coupled plasma mass spectrometry (Perkin Elmer ELAN 5000 A) and mercury analyses by cold vapor atomic fluorescence spectrophotometry (Brooks Rand), also at the University of Michigan Air Quality Laboratory. Landis and Keeler (1997) describe the laboratory techniques, method detection levels, and quality assurance and control for these analyses.

To calculate the average ambient air concentration of each metal, a concentration at or above the uncertainty was averaged as reported, and a concentration below the uncertainty was averaged as zero. Using 2000 over-water meteorological data, average deposition velocities of 0.00008 m/s and 0.0005 m/s were computed with the modified Williams model for fine and coarse particles, assuming that the aerodynamic diameters were 0.5 µm and 5 µm, respectively. Dry deposition rates $F_{metal-dry}$ (kg/year) for Tampa Bay were obtained from Equation 5, where $C_{metal-air}$ (ng/m³) was the average ambient air concentration of the metal, $v_{davg}$ (m/s) was the average deposition velocity and 31,536 was the appropriate units conversion factor for the annual dryfall loading of metals to the surface of Tampa Bay.

Equation 5. \[
F_{metal-dry} = 31,536 \cdot C_{metal-air} \cdot v_{davg}
\]

The wet deposition rates for each metal $F_{metal-wet}$ (kg/day) were determined as shown in Equation 6, where $C_{metal-rain}$ is the concentration of the metal in the rainfall (µg/L), $D$ is the depth of rainfall (mm), and 1.0 is a units conversion factor. $F_{metal-wet}$ for every day of rainfall was summed over the year to get the annual rainfall loading of metals to the surface of Tampa Bay.
Equation 6. \[ F_{\text{metal-wet}} = 1.0 \cdot C_{\text{metal-rain}} \cdot D \]

PCBs, PAHs and Organochlorine Pesticides

Field sampling

From March through October, 2001, ambient air samples of organochlorine pesticides and PAHs were collected at the Gandy Bridge site with a high volume sampler (Tisch Environmental, Inc.) operated at a flow rate of 225 l min\(^{-1}\) for 24-hours every 6\(^{th}\) day, on a schedule coincident with the National Air Monitoring System (NAMS) schedule for PM\(_{10}\). Identical to the USEPA Compendium Method TO-4A (1999) sampler, the sampler featured a total suspended particulate (TSP) inlet, and a 10-cm diameter quartz filter followed by a 6-cm x 10-cm piece of polyurethane foam (PUF). The sampler was positioned on top of a monitoring trailer and the sampler inlet height was ~4 m.

Daily PM\(_{2.5}\) and PM\(_{10-2.5}\) concentrations were available from a sequential dichotomous sampler also located at the Gandy Bridge site (Poor, et al., 2002). Daily surface weather observations from the National Weather Service Station at Tampa International Airport, ~10 km due north of the Gandy Bridge site, were obtained from the National Climatic Data Center website.

The pre-baked quartz filters (Whatman, Inc.) in aluminum foil within a sealed glass jar and the pre-cleaned PUFs (Supleco, Inc.) sealed in a glass jar within an aluminum canister were transported each week as needed in a cooler on blue ice from and to the Florida Department of Environmental Protection (FDEP) laboratory in Tallahassee and the EPCHC in Tampa, Florida. Prior to installation in and after removal from the air sampler, the quartz filters and PUFs were stored in a dark freezer at 4\(^{\circ}\)C.

For each day of sampling, the FDEP Organics Laboratory extracted the PCBs, PAHs, and organochlorine pesticides from the combined filter and PUF media, and analyzed the extracts with gas chromatography and either a mass spectrometer (PAHs) or an electron capture device (PCBs, organochlorine pesticides). Testing was done for 17 PCB congeners, 20 pesticides, and 16 PAHs.

Average ambient air concentrations were calculated for those organic air toxins with at least one concentration above the analytical lower detection level (LDL). Atmospheric deposition rates, however, were calculated only for those contaminants whose concentrations were above the LDL in 75% or more of the samples. For ambient air concentrations and atmospheric deposition rates, concentrations below the LDL were estimated as one-half of the LDL.

The general approach was to predict from ambient concentrations of organic toxins and from local meteorology both their wet and dry atmospheric loading to Tampa Bay. The model algorithms, which were adopted from current literature, predict based on the air temperature, wind speed, and the chemical properties of individual compounds the partitioning of these compounds between gas and particle phases, and their transfer between air and seawater or rainfall.
Laboratory Analyses

Polyurethane foam filters (PUFs) were pre-cleaned by the manufacturer. Additionally, PUFs were cleaned in the lab by sonication, first with a solution of 1:9 diethyl ether-hexane and followed three times with acetone. Quartz filters were prepared in the lab by heating at 450 °C for 6 hours. All the solvents used in the procedure were freshly distilled before use. After sampling, PUF and quartz filters were combined and Soxhlet-extracted for 18 hours with 160 ml of acetone. A final extract volume of 1 ml was split into two equal aliquots for PAH and organochlorine pesticide analyses. For pesticide analysis, the extract was GPC-cleaned on a 19 x 300 mm Waters Envirogel column. Part of this extract was additionally cleaned up with sulfuric acid. For each extraction batch were prepared and analyzed three quality-control (QC) samples for both PAH and pesticide analyses: an extraction blank, and two laboratory-fortified blanks. QC samples were prepared on a similar PUF used for sample collection. The extraction procedure was monitored using appropriate surrogates. Holding times of the samples after extraction did not exceed 40 days.

Samples were analyzed for selected PCBs and chlorinated pesticides (Tables 3 and 4) using a gas chromatograph and electron capture detector (GC-ECD) technique performed on two dissimilar fused silica capillary columns: 0.32 mm x 30m x 0.50 µm, 5% phenyl-substituted methylpolysiloxane stationary phase (DB-5, J & W Scientific) and a 0.32 mm x 30m x 0.50 µm, 50% phenyl-substituted methylpolysiloxane stationary phase (DB-608, J&W Scientific). Tetrachloro-m-xylene and decachloro-biphenyl were added to samples prior to extraction for use as surrogates. Most of parameters were analyzed in sulfuric acid-cleaned extracts except the ones non-resistant to this treatment: endosulfans, endrin and derivatives, dieldrin and methoxychlor for which GPC-cleaned extracts were used. For this study was used a HP6890 GC with splitless injections, helium as carrier gas and constant flow mode. Columns were temperature programmed from 80° C (for 1 min) at 30° C/min to 190° C (for 0 min) then at 3.6° C/min to 250° C (for 2.67 min) followed by 15° C/min to 280° C (for 5 min).

Sample extracts were analyzed for 16 PAHs (Table 8) using EPA Method 8270 for gas chromatography and mass spectrometry (GC/MSD) in the selective ion mode. Qualitative identification of the parameters in the extract was performed using the retention time and the relative abundance of two or three characteristic masses. Quantitative analysis was performed using an internal standard technique. Extraction efficiency was monitored using three surrogate standards. An HP6890 GC coupled with 5973 MSD was set up for splitless injections using helium as carrier gas in constant flow mode. Separation was achieved using a 30 m x 0.25 mm i.d. (film thickness 0.25 µm) DB-5MS capillary column. Injector and MS interface temperature: 280° C and oven temperature program: 50° C (for 1 min) at 30° C/min to 325° C (for 4 min). A selective ion mode 50 msec dwell time was used to monitor each ion.

Data Reduction

Average ambient air concentrations were calculated for those air toxins with at least one concentration above the analytical lower detection level (LDL). Atmospheric deposition rates, however, were calculated only for those contaminants whose concentrations were above the LDL
in 75% or more of the samples. For ambient air concentrations and atmospheric deposition rates, concentrations below the LDL were estimated as one-half of the LDL. The analytical LDL, recovery and precision for pesticides and PAHs are summarized in Tables 4 and 6, respectively.

For the organochlorine pesticides and the PAHs, the same approach was taken to predict from ambient concentrations and local meteorology the total atmospheric loading to Tampa Bay. Contaminant concentrations were converted to mole fraction at standard temperature and pressure as shown in Equation 7. Refer to Table 12 for the relevant physical and chemical properties of pesticides chlordane and endosulfan, and PAHs naphthalene, fluorene, anthracene, phenanthrene, fluoranthene and pyrene.

\[ X_i = \frac{RTC_i}{pM_i} \]  

Equation 7

where

\[ C_i = \text{ambient air concentration of contaminant } i, \text{ ng m}^{-3} \]
\[ T = \text{standard air temperature, 298 K} \]
\[ R = \text{ideal gas constant, 8.314 Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1} \]
\[ p = \text{standard pressure, 1.013 x 10}^5 \text{ Pa} \]
\[ M_i = \text{molecular weight, g mol}^{-1} \]
\[ X_i = \text{mole fraction of contaminant } i, \text{ ppb} \]

We assumed (1) that the particulate fraction of contaminant \( i \) was adsorbed onto ambient aerosols and directly related to the ambient aerosol surface area (Pankow, 1987), and (2) that the ambient aerosol surface area was reasonably represented by a collocated PM\(_{10}\) concentration (Equations 8 and 9). More typically, total suspended particulate (TSP) concentrations are an operational descriptor of aerosol surface area (Falconer and Harner, 2000). The distribution of contaminant \( i \) between gas and particle phase was computed by Equation 10 for pesticides and Equation 11 for PAHs (Finizio, et al., 1997). The gas fraction is 1-\( \phi \).

\[ \phi \cong \frac{C_{pi}PM_{10}}{C_{gi} + C_{pi}PM_{10}} \]  

Equation 8

\[ \phi \cong \frac{K_{pi}PM_{10}}{1 + K_{pi}PM_{10}} \]  

Equation 9

where

\[ K_{pi} = \frac{C_{pi}}{C_{gi}} \]
\[ C_{pi} = \text{particle phase concentration of contaminant } i, \text{ ng \( \mu \)g}^{-1} \text{ of aerosols} \]
\[ C_{gi} = \text{gas phase concentration of contaminant } i, \text{ ng m}^{-3} \]

\[ \log K_{pi} = -0.92\log p_{Li}^{0.6} - 5.63 \]  

Equation 10

\[ \log K_{pi} = -1.00\log p_{Li}^{0.6} - 5.47 \]  

Equation 11
Equation 12 describes the net gas flux across the air-water interface (Schwartzenbach, et al., 1993) where for contaminant \( i \), \( K_{OLi} \) = mass transfer velocity (cm s\(^{-1}\)), \( H_i \) = Henry’s Law constant (Pa m\(^3\) mol\(^{-1}\)), and \( C_{wi} \) = water concentration (mol m\(^{-3}\)). The mass transfer velocity at the air-water interface was estimated from Equation 13 (Hoff, et al., 1996), using the empirical relationships for \( k_{wi} \) and \( k_{ai} \) and the 10-m wind speed as given in Schwartzenbach, et al. (1995), Equations 14-18. Tampa Bay water concentrations for pesticides and PAHs were not available and were assumed to be \( \approx 0 \); also assumed was that at the surface, water temperature \( \approx \) air temperature. Henry’s Law constant was increased by 30% to account for salting-out effect of \(~0.4\) M salt water (Alaee, et al., 1996; Peng and Wan, 1998). Wind speeds measured at TIA were increased by 60% to better predict the wind speeds over the bay, based on our correlation of four years of hourly over water and TIA wind speeds.

\[
Flux_{gi} = K_{OLi} \left[ C_{wi} - \frac{C_{ai}}{H_i} \right] (1 - \phi) \\
\frac{1}{K_{OLi}} = \frac{1}{k_{wi}} + \frac{RT}{H_i k_{ai}} \\
k_{a,H2O} = 0.2 u_{10}^1 + 0.3 \\
k_{ai} = k_{a,H2O} (D_{ai} / D_{a,H2O})^{0.67} \\
k_{w,O2} = 4 \times 10^{-4} + 4 \times 10^{-5} u_{10}^2 \\
k_{wi} = k_{w,O2} (D_{wi} / D_{w,O2})^{0.5} \\
u_{10} = \left( \frac{10.4}{\ln z + 8.1} \right) u_z
\]

where

\( Flux_{gi} \) = net dry gas flux of contaminant \( i \)  \\
\( C_{ai} \) = ambient air concentration of species \( i \), Pa  \\
\( k_{wi} \) = water-side mass transfer coefficient for contaminant \( i \), s cm\(^{-1}\)  \\
\( k_{ai} \) = air-side mass transfer coefficient for contaminant \( i \), s cm\(^{-1}\)  \\
\( k_{a,H2O} \) = air-side mass transfer coefficient for water, s cm\(^{-1}\)  \\
\( k_{w,O2} \) = water-side mass transfer coefficient for oxygen, s cm\(^{-1}\)  \\
\( D_{ai} \) = air diffusion coefficient for contaminant \( i \), cm\(^2\) s\(^{-1}\)  \\
\( D_{wi} \) = water diffusion coefficient for contaminant \( i \), cm\(^2\) s\(^{-1}\)  \\
\( D_{a,H2O} \) = air diffusion coefficient for water, cm\(^2\) s\(^{-1}\)  \\
\( D_{w,O2} \) = water diffusion coefficient for oxygen, cm\(^2\) s\(^{-1}\)  \\
\( z \) = anemometer height, m  \\
\( u_z \) = wind speed at anemometer height, m s\(^{-1}\)
\( u_{10} = \text{wind speed at a height of 10 m, m s}^{-1} \)

To calculate the dry particle flux, we employed Equation 19 and ran an updated version of the William’s model (Williams, 1982) with one year of 30-minute Tampa Bay wind speed, air temperature, water temperature and relative humidity observations to obtain an average deposition velocity, assuming a particle diameter of 0.5 \( \mu \text{m} \).

\[
\text{Flux}_{pi} = \phi C_i V_d \quad \text{Equation 19}
\]

where

- \( \text{Flux}_{pi} = \text{dry particle flux of contaminant } i \)
- \( V_d = \text{average annual particle deposition velocity} = 0.0078 \text{ cm s}^{-1} \)

The scavenging of contaminants from the air to the water can be approximated by a washout ratio \( W = \frac{C_{\text{air}}}{C_{\text{water}}} \), where \( C_{\text{air}} \) and \( C_{\text{water}} \) are measured at the Earth’s surface (Seinfeld and Pandis, 1998) and \( W_{gi} \) and \( W_{pi} \) represent the washout ratios for the gaseous and particle form of the \( i^{\text{th}} \) contaminant, respectively. Like dry deposition, wet deposition has both a gas and a particle component (Equation 20). Washout ratios are given in Table 15. A \( W_{pi} \) value of \( \sim 10^5 \) was adopted for particle-phase contaminants, based on current literature (Halsall, et al., 2001; Poster and Baker, 1996). The partitioning of contaminant gases into rainfall was approximated with Henry’s Law at 25 \( \text{oC} \), as shown in Equation 21.

\[
\text{Flux}_{\text{wet},i} = \left[ W_{gi}(1-\phi) + W_{pi}\phi \right] \text{precipitation rate} \quad \text{Equation 20}
\]

\[
W_{gi} = \frac{RT}{H_i} \quad \text{Equation 21}
\]

To investigate temperature-dependence, we prepared for each contaminant a Clausius-Clayton plot of \( \ln P \) versus \( 1/T \) (Equation 22), and from the slope of this plot we calculated the reaction enthalpy (\( \Delta H \)).

\[
\ln P = -\frac{\Delta H}{RT} + \text{constant} \quad \text{Equation 22}
\]
### Application of a Thermodynamic Model to Coarse and Fine Mode Aerosols at a Tampa Bay Coastal Site

Melissa Evans, Paul Tate, Noreen Poor and Scott W. Campbell  
Proceedings of the 94th Annual Air & Waste Management Conference and Exhibition, held June 24-28, 2001, in Orlando, FL.  
Available on the TBADS Final Report September 2002 CD.

The application of a thermodynamic model for aerosol-gas equilibrium to aerosols near coastal sites presents a challenge due to mixing of urban and marine aerosols, and the transfer of volatile species between them. At such locations, it has been observed that most of the nitrate and chloride are partitioned into the coarse fraction (diameter > 2.5 µm) of the aerosol particles while most of the ammonium is present in the fine fraction (diameter < 2.5 µm). The fact that concentrations of the various ions are not uniform across the aerosol size distribution has implications to the measurement and calculation of chemical deposition. In this work, we assume that both the coarse and fine mode aerosols are in equilibrium with the gas phase and apply the thermodynamic part of AIM (Aerosol Inorganics Model) to study the distribution of nitrate, ammonium, and chloride ions between the two fractions. Model calculations are in qualitative agreement with measurements taken at the Gandy Bridge site in Tampa, FL.

### Atmospheric Deposition and Source Apportionment of Toxic Metals To the Tampa Bay Estuary

Julie K. Earls, Noreen D. Poor, John M. Ondov  
Proceedings of the 94th Annual Air & Waste Management Conference and Exhibition, held June 24-28, 2001, in Orlando, FL.  
Available on the TBADS Final Report September 2002 CD.

The purpose of this research is to investigate toxic metal (1) ambient air concentrations, (2) fluxes to Tampa Bay and (3) source apportionment. Multiple 24-hour PM (fine and coarse) samples were acquired on 47-mm diameter PTFE filters with a Rupprecht & Patashnick Partisol Dichotomous Sequential air sampler throughout the months of January, February and March 2000 at the Environmental Protection Commission of Hillsborough County Gandy Bridge monitoring site in Tampa, FL. The filters were analyzed by XRF for 42 metals, ion chromatography for \( \text{SO}_4^{2-}, \text{NO}_3^- \) and \( \text{NH}_4^+ \) and thermal/optical analysis for PM\(_2.5\) EC/OC (elemental carbon/organic carbon) quantities present. Fluxes for each metal are calculated from a deposition velocity derived from the “Williams” model by researchers at the University of Maryland for the Tampa Bay Estuary Program. Source profiles were obtained from the EPA database, SPECIATE for input into the model. Data were analyzed for one day during this time period using the CMB8 (Chemical Mass Balance 8) model to estimate the largest contributing sources impacting the receptor site. Local meteorological and trajectory analyses were gathered to enhance source apportionment. Results of deposition of toxic metals to Tampa Bay Estuary were 1.8 kg/yr Cr, 3.5 kg/yr Ni, 13.2 kg/yr Cu, 18.0 kg/yr Zn and 7.0 kg/yr Pb. In the coarse fraction, source apportionment found seven sources as follows: 37% NaCl, 27% Heavy Duty Diesel Vehicles, 15% Cement Kiln, 12% Fertilizer Industry – Phosphate Production, 5% Lime Dust, 5% Soil and 17% unknown origin. In the fine fraction, source apportionment found eight sources as follows: 34% Ammonium Bisulfate, 30% Fireplaces (softwoods burning), 14% Resource Recovery Facility, 13% Ammonium Nitrate, 4% Crude Oil Boiler, 1% Cement Dust, 1% Light Duty Vehicles (non-catalyst) and 3% unknown.
### Scrubbing of Atmospheric Nitric Acid and Sulfuric Acid by Marine Air

Melissa C. Evans, Noreen D. Poor

Proceedings of the 94th Annual Air & Waste Management Conference and Exhibition, held June 24-28, 2001, in Orlando, FL.

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Size distributions of particulate nitrate and sulfate were measured at a bayside monitoring site using an Andersen cascade impactor and a dichotomous sampler to determine the impact of sea-salt in scrubbing the atmosphere of nitric and sulfuric acids. Nitrate was dominant in the coarse fraction, while sulfate was in the fine. Comparisons with sodium reveal the distinct correlation of nitrate with sodium. Sulfate appeared to be closely affiliated with ammonium in the fine fraction. Chloride depletion was calculated, showing a high chloride depletion rate during the sampling period. Gravitational settling flux was calculated for three major size fractions to determine the impact of sea-salt on the shifting of the mode of nitrate from fine to coarse. Results revealed an increase of over 60 times in the settling velocity.

### A Comparison of Modeled and Actual SO₂ Concentrations in the Tampa Bay Estuary Using the CALMET/ CALPUFF Modeling System

Gordon R. Hannaway, Ali Kamal, Ken Sturrock, Noreen D. Poor

Proceedings of the 94th Annual Air & Waste Management Conference and Exhibition, held June 24-28, 2001, in Orlando, FL.

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As part of the Tampa Bay Estuary Program (TBEP) atmospheric deposition study (TBADS) we have an interest in (1) how representative SO₂ concentration data from the Gandy Bridge TBADS monitoring site are for the entire Tampa Bay Estuary and (2) how well CALMET/CALPUFF models SO₂ concentrations. Approximately 70% of the atmospheric sulfur deposition to the Tampa Bay Estuary is from dry deposition of SO₂ gas.¹ The modeling domain is Central Florida: 400 x 330 km with a 5 km grid scale and a 2 km receptor grid scale of the entire Bay area (most of Hillsborough and Pinellas counties).² We have chosen May 2000 for modeling because ozone concentrations are higher and thus the SO₂ transformation rate is higher. Meteorological (upper air, precipitation, and surface) data from the National Climatic Data Center and buoy data from the NOAA Physical Oceanographic Real-Time System are input to CALMET. The 1996 National Emissions Inventory provided the point source emissions rates. Twelve SO₂ monitors throughout Hillsborough and Pinellas counties were polled for the air quality data. Preliminary data show a general agreement for the concentration isopleths but modeled plumes had SO₂ concentrations 3 to 4 times greater than observed concentrations. Surfer 7th interpolates and grids by kriging modeled and measured data. Our analysis compares for a monthly average and for weekly averages actual and modeled spatial SO₂ concentration data.
<table>
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<tr>
<th><strong>An Experiment to Measure NO, and SO₂ Transformation Rates</strong></th>
<th>NO₃ and SO₂ transformation rates are important in determining total annual nutrient loading to Tampa Bay, FL. This paper outlines both the experimental approach planned for better determining these transformation rates in a coastal environment and the data quality objectives (DQO) process followed during project design. Plumes of three local power plants will be utilized to assess ambient transformation rates, and the sampling array will include sites to determine background concentrations. The sampling design instrumentation will include: Opsis® DOAS UV-spectrometer open path monitoring, URG© sequential annular denuder system, nephelometer, wind speed, wind direction, relative humidity and UV-flux measurements. A data quality objectives (DQO) process was used to determine the optimum siting to capture source emissions plumes without sacrificing information required to quantify transformation rates. Transformation rates are currently modeled using CALPUFF/CALMET (MESOPUFF II algorithm), but peer review indicates that MESOPUFF II can underestimate SO₂ transformation rates for a humid environment. Tampa monitored versus modeled results support this conclusion. The transformation rates directly affect nutrient deposition rates to the Bay because transformed products have deposition rates that vary from that of the original constituents.</th>
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<tr>
<td>Kerstin Lesley Kenty, Noreen D. Poor, Scott W. Campbell</td>
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<td>Proceedings of the 94th Annual Air &amp; Waste Management Conference and Exhibition, held June 24-28, 2001, in Orlando, FL.</td>
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<tr>
<td><strong>Ammonia Flux at the Air/Water Interface of Tampa Bay</strong></td>
<td>Recent nitrogen deposition research in the Tampa Bay Estuary indicates that ammonia deposition dominates the total dry nitrogen flux to the bay. Gaseous plus aerosol ammonia contribute approximately 450 tons per year or 60% of the total nitrogen deposition of 760 tons per year to the estuary. To further understand the effects of ammonia deposition on the health of Tampa Bay, a research study is underway to quantify the flux of ammonia at the air/water interface. Flux measurements were derived from air and water monitoring data that was collected for six days from January 11–17, 2002. Monitoring equipment was placed on the Gandy Bridge seawall located adjacent to Tampa Bay just west of the City of Tampa. The NOAA inferential buoy model, which solves a set of simultaneous turbulence equations to obtain transfer coefficients that describe heat transfer across the water surface, was utilized to calculate the gas and particle deposition velocities. Gaseous and aerosol ammonia concentrations were measured with a URG, Inc., Annular Denuder System (ADS) and grab samples from the bay were analyzed in the laboratory for daily ammonium concentrations. From collocated measurements of wind speed and direction, air and water temperature, air and water ammonia and ammonium concentrations, relative humidity, water pH and salinity, a direction and magnitude for the ammonia flux was derived. From January 11-17, 2002, the average flux of ammonia at the interface was –0.00972 kg/ha/day, indicating that ammonia was emitted from the bay to the airshed. Over the 6-day monitoring period, ammonia was deposited to the bay for 3 days and emitted from the bay for 3 days. For 2 of the 3 days that ammonia was emitted from the bay, it is suspected that a continuous rainfall event contributed to fertilizer runoff to the bay, causing excessive ammonium concentrations at the sampling site.</td>
</tr>
<tr>
<td>Connie A. Mizak, Noreen D. Poor</td>
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<td>Available on the TBADS Final Report September 2002 CD.</td>
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### The Influence of Air Mass Origin on Wet Deposition of Nitrogen to Tampa Bay, FL

R. David Smith Jr., Noreen D. Poor, Arlene G. Laing


*Available on the TBADS Final Report September 2002 CD.*

The objective of this study was to determine the variation in the capacity of an air mass to deliver nitrogen to Tampa Bay through wet deposition processes. NADP AIRMoN precipitation chemistry data was first obtained and rainfall events were sorted into groups according to area of origination. Air masses were categorized first based upon HYSPLIT back trajectories, and then by chemical classifications. Trajectory analysis showed that nitrate N-flux was the greatest from slow-moving trajectories local to Tampa at 0.049 kg/ha/d, followed by other terrestrial-originating trajectories including Bahamas at 0.041 kg/ha/d, and Cape at 0.034 kg/ha/d. Cuba, Gulf, and Panhandle trajectories, which typically originated in the Gulf of Mexico and encountered land only near the monitoring site, had the lowest nitrate N-fluxes at 0.022, 0.026, and 0.031 kg/ha/d, respectively. The pattern of ammonium N-flux contribution was lower, but closely resembled that of nitrate N-flux with terrestrial trajectories higher than maritime trajectories. Tampa trajectories, however, showed slightly lower than average ammonium N-flux at 0.02 kg/ha/d. Upon chemical classification, we discovered that local combustion sources contribute the highest nitrate N-flux at 0.053 kg/ha/d, while the lowest average fluxes were again contributed by marine air masses with 0.023 and 0.018 kg/ha/d for nitrate and ammonium, respectively. Terrestrial aged combustion sources typically moved east to west across the state and contributed the highest ammonium flux at 0.033 kg/ha/d, while the flux of nitrate for aged terrestrial air masses was below the average at 0.024 kg/ha/d. In general, marine air masses were determined to be “cleaner” with respect to their tendency to deposit nitrogen through wet deposition processes, while local combustion was found to contribute the highest overall nitrogen flux dominated by nitrate deposition from local combustion sources.

### Can Bulk Deposition Measurements Reasonably Estimate Nitrogen Deposition Rates?

Heather C. Hendrix, Noreen D. Poor


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Earlier studies have focused primarily on the inorganic fraction of nitrogen, including nitric acid and nitrate, ammonia and ammonium, in estimating deposition rates to surface waters. This research investigates the contribution of organic amines to the directly measured flux of organic amines and inorganic ammonium. A polycarbonate funnel with a 12.2-cm diameter, and attached to a 2-L polyethylene bottle via Teflon tubing comprised the bulk collector. Subsamples of an acid wash of the funnel and bottle were analyzed for Kjeldahl nitrogen and for ammonium nitrogen, and the difference in mass assigned to organic amines. The organic amines contributed ~70% to the total organic amine and inorganic ammonium. For comparison, an alternative method was to infer the dry deposition of ammonia/ium from their ambient air concentrations, obtained from a collocated annular denuder system. In the comparison, direct deposition was ~10% higher than the inferred deposition, and this difference can be attributed to the organic amine nitrogen.

### Do Macroparticles Contain Nitrogen?

Melissa C. Evans, Heather Hendrix-Holmes, Noreen D. Poor


In recent years, aerosol equilibrium modeling has predicted, and speciated size-distributed monitoring has confirmed, the presence of coarse particle nitrogen. Coarse particles of sodium nitrate can form, for example, when a marine air mass laden with sodium chloride mixes with an anthropogenic air mass rich in nitric acid. These coarse particles are typically less than 10 µm. The purpose of this investigation is to determine if rapidly depositing atmospheric particles or particle aggregates with diameters from 10 to 80 µm contain nitrogen. During a six-week period in October and November 2001,
daily 24-hour integrated particle samples were collected on 46.2-mm diameter PTFE filters at a flow rate of 28.3 L min⁻¹ using an inverted filter pack with a straight inlet. A co-located sequential dichotomous sampler and an annular denuder system provided estimates of the contributions of nitric acid, ammonia, PM₁₀ and PM₂.₅ on the macroparticle filter. A co-located Andersen cascade impactor provided size-specified nitrate and ammonium concentrations for particles up to 10 µm in diameter. Results did reveal the presence of nitrate on the macroparticle fraction, which corresponded to higher than average Ca²⁺ and HNO₃ concentrations. Nitric acid bias was estimated to be ~30% of the TSP fraction when compared to the dichotomous fraction.

We report on the results of a series of CALPUFF model simulations considering different modeling domain (computational grid) sizes to evaluate the errors associated with the loss of pollutant mass at the edge of the computational grid boundary. For the simulations, we chose four different computational grid sizes of 400 km x 330 km, 325 km x 250 km, 275 km x 200 km, and 250 km x 175 km. The largest computational grid (400 km x 330 km) was treated as the baseline to which all others were compared. To reduce the processing time, we used two months of 1990 Tampa International Airport hourly surface weather observations prepared as Industrial Source Complex (ISC) meteorological input data. Percent error from baseline was calculated at each grid point located within a subdomain of 250 km x 175 km for concentrations, and wet and dry deposition rates of NOₓ, nitric acid and nitrate. The error analyses were done for 5, 10, and 13 volume sources, with the largest volume emissions modeled first. Average percent error ranged from 3% to 28%, 3% to 30%, and 12% to 46% for concentration, dry deposition rates and wet deposition rates, respectively, of modeled nitrogen species. The average percent error increased with additional volume sources (see Table 2) and as the computational domain size approached the 100 km x 60 km receptor subdomain. Errors were not symmetrical, and suggest that not only the atmospheric residence time of each of the modeled species, but the source locations or predominant wind direction may also be important in defining the computational grid.
The average total (wet plus dry) nitrogen deposition to the Tampa Bay Estuary was 7.3 (± 1.3) kg-N ha$^{-1}$ yr$^{-1}$ or 760 metric tons-N yr$^{-1}$ for August 1996-July 1999, estimated as a direct deposition rate to the 104,000-ha water surface. This nitrogen flux estimate accounted for ammonia exchange at the air-sea interface. The uncertainty estimate was based on measurement error. Wet deposition was 56% of the total nitrogen deposition over this period, with an average 0.78 ratio of dry-to-wet deposition. Wet nitrogen deposition rates varied considerably, from near zero to 1.3 kg-N ha$^{-1}$ month$^{-1}$. About 40% of the total nitrogen flux occurred during the summer months of June, July and August when rainfall was the highest, except for 1997-1998 when the El Niño phenomenon brought unseasonal rainfall. Ammonia/ammonium contributed to 58%, and nitric acid/nitrate 42%, to the total nitrogen deposition over the 3-year period. In one summer as waters of Tampa Bay warmed above 28°C and ammonium concentrations reached 0.03 mg l$^{-1}$, the estimated net flux of ammonia was from the Bay waters to the atmosphere.

For over one year, the Environmental Protection Commission of Hillsborough County (EPCHC) in Tampa, Florida, operated two dichotomous sequential particulate matter air samplers collocated with a manual Federal Reference Method (FRM) air sampler at a waterfront site on Tampa Bay. The FRM was alternately configured as a PM$_{2.5}$, then as a PM$_{10}$ sampler. For the dichotomous sampler measurements, daily 24-hour integrated PM$_{2.5}$ and PM$_{10-2.5}$ ambient air samples were collected at a total flow rate of 16.7 L min$^{-1}$. A virtual impactor split the air into flow rates of 1.67 L min$^{-1}$ and 15.0 L min$^{-1}$ onto PM$_{10-2.5}$ and PM$_{2.5}$ 47-mm diameter PTFE® filters, respectively. Between the two dichotomous air samplers, the average concentration, relative bias and relative precision were 13.3 μg m$^{-3}$, 0.02% and 5.2% for PM$_{2.5}$ concentrations ($n=282$), and 12.3 μg m$^{-3}$, 3.9% and 7.7% for PM$_{10-2.5}$ concentrations ($n=282$). FRM measurements were alternate day 24-hour integrated PM$_{2.5}$ or PM$_{10}$ ambient air samples collected onto 47-mm diameter PTFE® filters at a flow rate of 16.7 L min$^{-1}$. Between a dichotomous and a PM$_{2.5}$ FRM air sampler, the average concentration, relative bias and relative precision were 12.4 μg m$^{-3}$, -5.6% and 8.2% ($n=43$); and between a dichotomous and a PM$_{10}$ FRM air sampler, the average concentration, relative bias and relative precision were 25.7 μg m$^{-3}$, -4.0% and 5.8% ($n=102$). The PM$_{2.5}$ concentration measurement standard errors were 0.95, 0.79 and 1.02 μg m$^{-3}$; for PM$_{10}$ the standard errors were 1.06, 1.59, and 1.70 μg m$^{-3}$ for two dichotomous and one FRM samplers, respectively, which indicate the dichotomous samplers have superior technical merit. These results reveal the potential for the dichotomous sequential air sampler to replace the combination of the PM$_{2.5}$ and PM$_{10}$ FRM air samplers, offering the capability of making simultaneous, self-consistent determinations of these particulate matter fractions in a routine ambient monitoring mode.
Predictions of Size-Resolved Aerosol Concentrations of Ammonium, Chloride and Nitrate at a Bayside Site Using EQUISOLV II

Scott W. Campbell, Melissa C. Evans, and Noreen D. Poor


For a reprint, please contact Campbell@eng.usf.edu.

Measured ambient air concentrations of ammonium, chloride and nitrate were compared with concentrations produced by EQUISOLV II, an aerosol thermodynamic equilibrium model. The monitoring equipment was located ~50 m from Old Tampa Bay at the eastern end of the Gandy Bridge in Tampa, Florida. Size-segregated ion concentrations of ammonium, sodium, potassium, calcium, magnesium, fluoride, chloride, nitrite, nitrate, sulfate and phosphate were determined from 6-day and 1-day integrated cascade impactor samples obtained in May and August 2001, respectively. EQUISOLV II was initialized with these ion concentrations by size bin, and by gas phase concentrations of the volatile species, acquired with a collocated annular denuder system. The model redistributed the ions between the size bins until gas and particle concentrations reached equilibrium. The model calculated predominantly fine particle ammonium and coarse particle chloride and nitrate. For the May sampling period, when the average relative humidity was below 65%, the model predicted the formation of seven solids KNO3, K2SO4, (NH4)2SO4, Na2SO4, NaCl, NaNO3, and CaSO4·2H2O. The amounts of ammonium in the fine fraction and of nitrate and chloride in the coarse fraction were predicted within the combined measurement and modeling uncertainty in the majority of cases.

Assimilation of Nitrogen Isotope Data and Source Recognition in the Tampa Bay Estuary

Julie K. Earls

Thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Public Health, Department of Environmental and Occupational Health, College of Public Health, University of South Florida

August 2001

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The objective of this research was to determine whether the sources of nitrogen in the Tampa Bay Estuary were anthropogenic or natural by using nitrogen isotope (δ¹⁵N) data assimilation. Wet nitrogen isotope data were collected during the period of 7 July 1998 to 4 October 1999 at the Gandy site in Hillsborough County. Dry nitrogen isotope data was collected as well from 4 February 1999 to 26 November 1999. Ambient air concentrations (Total N) and rainfall concentrations (NH₄⁺ and NO₃⁻) from the Gandy site were compared to δ¹⁵N values collected. Trajectory and graphical analyses revealed the most enriched values for δ¹⁵N nitrate and ammonium occur with southerly winds, albeit the lower average rainfall concentrations. Perhaps the ocean or estuary is the natural sources of this enriched δ¹⁵N. The trajectory and graphical analyses also revealed that the most depleted δ¹⁵N nitrate and ammonium occurred when the air mass came from the southeast at higher rainwater concentrations. This suggests under these wind conditions the agricultural and inorganic fertilizer manufacturing contributed more to atmospheric nitrogen. Close to 0‰ values for precipitation δ¹⁵NO₃⁻ are associated with greater NO₃⁻ concentration values, indicating influence of combustion from cars and power plants. This is supported by the fact that the higher concentrations on the dry ADS filters are closer to 0‰ isotopic values.
Ammonia Sampling Using the Ogawa® Passive Sampler

Paul Tate

Thesis submitted in partial fulfillment of the requirements for the degree of Master of Science, Department of Chemistry, College of Arts and Sciences, University of South Florida

March 2002

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The purposes of this research were to determine the efficacy of using the Ogawa® passive sampling device (PSD) to measure ammonia and to identify significant sources of ammonia adjacent to Hillsborough and Tampa Bay. Ninety four samplers were deployed over a 180-km² area for two weeks in October 2001. Within the area sampled were located suburbs, an urban center, major highways, port activities, fertilizer manufacturing, wastewater treatment, coal-combustion power plants, warehousing and dairy farming. The sampled locations were arranged in a triangular grid pattern spaced 1.5 km apart. The pattern was designed to locate circular hot spots with a medium radius of 0.75 km. The minimum, maximum, mean and median ammonia concentrations were 0.06, 15, 2.0 and 1.5 µg/m³, respectively, and the estimated precision was 16%. Hot spots identified from kriged concentration data coincided with inventoried ammonia sources. The relative bias and precision of the PSD based on collocation with an annular denuder system were ±30% and 20%.

Ammonia Gas Emissions from a Tampa Bay Area Wastewater Treatment Plant

Scott A. Mower

Thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Public Health, Department of Environmental & Occupational Health, College of Public Health, University of South Florida

May 2002

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Estimates of ammonia gas (NH₃) emissions were made for a Tampa Bay area wastewater treatment plant that utilized activated sludge and lime stabilization processes for wastewater and sludge treatment, respectively. Ogawa® passive sampling devices (PSDs), annular denuders systems (ADS), and impingers were used to sample NH₃. An active sampling apparatus (ASA) was employed for over-basin NH₃ sampling. This apparatus was equipped with ADS for NH₃ gas capture and featured a supply air NH₃ removal system and an isolated enclosure for water to air NH₃ gas transfer. ASA sampling was performed at basins where quantifiable ammonium concentrations were detected from wastewater grab sample ion chromatograph (IC) analysis. These basins were the headworks, fermentation, first anoxic, aeration, and second anoxic basins. The respective mean over-basin ambient air NH₃ concentrations were 68 µg m⁻³, 6 µg m⁻³, 6 µg m⁻³, 140 µg m⁻³, and 100 µg m⁻³. The predicted annual output from the wastewater treatment basins based on a simple box model and ASA results was 2.6 x 10⁻³ metric tons yr⁻¹, a fraction of the 5 metric tons yr⁻¹ output predicted from the Carnegie Mellon University Ammonia Emissions Inventory. NH₃ concentrations inside the sludge treatment facility (STF) were determined from IC analysis of PSD and impinger samples. The mean daily NH₃ concentration was 2,800 µg m⁻³ and varied from 30 µg m⁻³ to 8,400 µg m⁻³. The STF theoretical annual output based on a simple box model was 0.5 (±0.6) metric tons yr⁻¹. The STF release rate and total annual output was also estimated from the AERMOD air dispersion model and was 0.008 g s⁻¹ m⁻² or 0.8 (±0.4) metric tons yr⁻¹, respectively. Results from an on-site PSD sampling grid showed no distinctive NH₃ emission signature for the wastewater treatment basins but revealed a distinctive plume from the STF.
BRACE Research Objectives

1. How do concentrations and fluxes of nitrogen species vary with time and space?

2. What is the total nitrogen budget?

3. How does the marine environment influence nitrogen deposition?

4. How is nitrogen exchanged at the air-sea interface?

5. How well do direct measurements of nitrogen compare with modeled fluxes?

6. What are the regional ammonia emissions?

7. How sensitive are deposition models to input data and parameterization?

8. In what proportions do mobile, stationary and area sources contribute to nitrogen loading to Tampa Bay?

9. What impact will the Gannon Station re-powering have on nitrogen deposition?
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<th>Properties at 25 °C</th>
<th>$M_i$, Molar Weight</th>
<th>$\rho_{li}$, Vapor Pressur</th>
<th>$H_i$, Henry’s Law Constant</th>
<th>$D_{ai}$, Diffusivity in Air</th>
<th>$D_{wi}$, Diffusivity in Water</th>
<th>$W_{gi}$, Gas Scavenging Coefficient</th>
<th>$W_{pi}$, Particle Scavenging Coefficient</th>
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<td>2000</td>
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</table>

\(^a\) ATSDR, Toxicological Profiles, 2002
\(^b\) Shui and MacKay, 1997
\(^c\) www.epa.gov/superfund/resources/soil, November 26, 2001
\(^d\) Gustafson, 1994.
\(^e\) Calculated from RT/H, R = 8.314 Pa m^3 mol^{-1} K^{-1}
\(^f\) From Halsall, et al., 2001; Poster and Baker, et al., 1999