Ammonia Flux At The Air/Water Interface Of Tampa Bay

by

Constance Anne Mizak

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Civil Engineering Department of Civil and Environmental Engineering College of Engineering University of South Florida

Major Professor: Noreen D. Poor, Ph.D.
Scott W. Campbell, Ph.D.
Robert P. Carnahan, Ph.D.
Mark E. Luther, Ph.D.
Robert J. Murphy, Ph.D.

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DEDICATION

This dissertation is dedicated to my husband, John C. Mizak, who has continually provided unconditional love, support, guidance and encouragement throughout my pursuit of the doctoral degree.
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<tr>
<td>$\psi$</td>
<td>Panofsky’s function</td>
</tr>
<tr>
<td>A</td>
<td>area</td>
</tr>
<tr>
<td>ADS</td>
<td>annular denuder system</td>
</tr>
<tr>
<td>AIRMoN</td>
<td>Atmospheric Integrated Research Monitoring Network</td>
</tr>
<tr>
<td>aq</td>
<td>aqueous</td>
</tr>
<tr>
<td>$\beta$</td>
<td>scavenging coefficient</td>
</tr>
<tr>
<td>BRACE</td>
<td>Bay Regional Atmospheric Chemistry Experiment</td>
</tr>
<tr>
<td>C</td>
<td>concentration</td>
</tr>
<tr>
<td>$^\circ$C</td>
<td>degrees Celsius</td>
</tr>
<tr>
<td>$C_d$</td>
<td>drag coefficient</td>
</tr>
<tr>
<td>cm</td>
<td>centimeter</td>
</tr>
<tr>
<td>CMU</td>
<td>Carnegie Mellon University</td>
</tr>
<tr>
<td>$c_p$</td>
<td>specific heat of air</td>
</tr>
<tr>
<td>d</td>
<td>day</td>
</tr>
<tr>
<td>$D_H$</td>
<td>dimensionless heat transfer coefficient</td>
</tr>
<tr>
<td>DST</td>
<td>daylight savings time</td>
</tr>
<tr>
<td>$D_p$</td>
<td>drop diameter</td>
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<tr>
<td>$D_w$</td>
<td>dimensionless moisture transfer coefficient</td>
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ε  error
E  moisture flux
EPA  Environmental Protection Agency
EPCHC  Environmental Protection Commission of Hillsborough County
EPCRA  Emergency Planning and Community Right to Know Act
F  flux
FPL  Florida Power & Light Company
Gg  gigagrams
H  Henrys Law constant
H  sensible heat flux
ha  hectare
HNO₃  nitric acid
H₂O  water
H₂SO₄  sulfuric acid
I  rainfall intensity
IC  ion chromatography
k  von Karman's constant
K  dissociation constant
K  Kelvin
Kₑ  mass transfer coefficient
kg  kilogram
km  kilometer
L     liter
L     Obukhov length scale
LE    moisture flux
LEPC  Local Emergency Planning Commission
m     meter
min   minute
mg    milligram
ml    milliliter
mm    millimeter
M     molecular mass
MSL   mean sea level
Mt    metric ton
MΩ    megaohm
n     number of samples
ng    nanogram
N     nitrogen
NADP  National Atmospheric Deposition Program
NAMS  National Ambient Monitoring System
N_p   droplet size distribution
NH_3  ammonia
NH_4^+ ammonium ion
NH_x  total ammonia (ammonia+ammonium)
<table>
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<th>Acronym</th>
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<tr>
<td>NOAA</td>
<td>National Oceanic and Atmospheric Administration</td>
</tr>
<tr>
<td>NO\textsubscript{x}</td>
<td>nitrogen oxides</td>
</tr>
<tr>
<td>$\rho$</td>
<td>air density</td>
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<tr>
<td>P</td>
<td>probability</td>
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<tr>
<td>PCA</td>
<td>Principle Components Analysis</td>
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<tr>
<td>POTW</td>
<td>Publicly Owned Treatment Works</td>
</tr>
<tr>
<td>q</td>
<td>specific humidity</td>
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<tr>
<td>r</td>
<td>resistance</td>
</tr>
<tr>
<td>R</td>
<td>Universal Gas Constant</td>
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<tr>
<td>R\textsuperscript{2}</td>
<td>coefficient of determination</td>
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<td>relative humidity</td>
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<td>second</td>
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<td>S</td>
<td>salinity</td>
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<td>standard deviation</td>
</tr>
<tr>
<td>SERC</td>
<td>State Emergency Response Commission</td>
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<td>SO\textsubscript{2}</td>
<td>sulfur dioxide</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
</tr>
<tr>
<td>$\tau$</td>
<td>momentum flux</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
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<tr>
<td>TBEP</td>
<td>Tampa Bay Estuary Program</td>
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<tr>
<td>TECO</td>
<td>Tampa Electric Company</td>
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<tr>
<td>TMDL</td>
<td>Total Maximum Daily Load</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>TPQ</td>
<td>Threshold Planning Quantity</td>
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<td>TRI</td>
<td>Toxics Release Inventory</td>
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<tr>
<td>µg</td>
<td>microgram</td>
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<tr>
<td>µm</td>
<td>micrometer</td>
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<tr>
<td>$U_t$</td>
<td>terminal velocity of a drop</td>
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<td>$u_r$</td>
<td>friction velocity</td>
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<td>$u_z$</td>
<td>wind speed</td>
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<td>V</td>
<td>volume</td>
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<td>deposition velocity</td>
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<td>volume/volume</td>
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<tr>
<td>w</td>
<td>vertical wind velocity</td>
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<td>weight/volume</td>
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<td>WD</td>
<td>wind direction</td>
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<tr>
<td>$W_{NH3}$</td>
<td>rate of transfer of a gas to a falling raindrop</td>
</tr>
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<td>WS</td>
<td>wind speed</td>
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<td>$\gamma$</td>
<td>activity coefficient</td>
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<td>yr</td>
<td>year</td>
</tr>
<tr>
<td>z</td>
<td>height</td>
</tr>
<tr>
<td>$z_H$</td>
<td>roughness length for heat</td>
</tr>
<tr>
<td>$z_W$</td>
<td>roughness length for moisture</td>
</tr>
<tr>
<td>$z_o$</td>
<td>roughness length for momentum</td>
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AMMONIA FLUX AT THE AIR/WATER INTERFACE OF TAMPA BAY

Constance Anne Mizak

ABSTRACT

An ammonia emissions inventory discovered that 90% of the ammonia emitted from Pinellas, Hillsborough, and Polk counties, originated from the latter two counties. This finding is significant and suggests that a substantial portion of the ammonia deposited to Tampa Bay is transported with easterly air masses.

Ammonia and ammonium concentrations at the coastal Gandy Bridge site were seasonally and diurnally consistent, but the rural Sydney site showed greater variability. It was determined that wind direction was the most influential parameter affecting the Gandy Bridge site, which supports the hypothesis that an advection of ammonia from the east is a major source of ammonia to the estuary. Sequential sampling of ammonium in wet deposition at the Gandy Bridge site confirmed that between 35% and 60% of the ammonium \( (C_{NH4}) \) in rainfall is deposited to Tampa Bay during the initial 20% of precipitation \( (D) \) according to the power law, \( C_{NH4} = aD^{-b} \). Ammonium concentrations were predicted with an aqueous-phase accumulation model and a relationship between \( I \), rainfall intensity in mm min\(^{-1}\) and \( \beta \), scavenging rate in min\(^{-1}\) was shown as \( \beta = 0.08I^{0.66} \). This algorithm will facilitate future modeling studies that explore the relationship
between the wet deposition of ammonium and ammonia reduction strategies in Tampa Bay.

The NOAA Buoy model accurately predicts sensible heat flux, and is an effective tool for estimating the offshore air/water exchange rates of ammonia over Tampa Bay. If near-shore vs. offshore meteorological measurements are used, the model under-predicts flux parameters by as much as 30% in the summer season. The model was “calibrated” to correct this deficiency.

Bi-directional ammonia flux measurements during the fall and winter seasons resulted in an average flux rate of 96.2 µg-NH$_3$ m$^{-2}$ d$^{-1}$, indicating a net transfer from air to water. During the 2003 summer season, an average ammonia flux rate of -117.9 µg-NH$_3$ m$^{-2}$ d$^{-1}$ and a 32% reduction in the annual ammonia dry deposition rate to Tampa Bay was calculated. Wet deposition likely contributes to ammonia reemission from the estuary. These results indicate that volatilization of ammonia reduces the nitrogen burden available for biological synthesis in Tampa Bay.
CHAPTER 1
INTRODUCTION

1.1 Purpose of the Study

The objectives of this research were to provide more accurate estimates of the quantity and temporal patterns of ammonia loading from the atmosphere to Tampa Bay, to determine if estuarine meteorological conditions cause a bi-directional ammonia flux to the bay, and to explore the variation between measured data and modeled fluxes to reduce or explain any observed error.

Ammonia can be extremely detrimental to the ecology of an estuary because it is the preferred source of nitrogen for phytoplankton (Day et al., 1989). Increasing primary productivity caused by nutrient enrichment is the principal cause of estuarine eutrophication, a condition that can lead to hypoxic and anoxic conditions in water bodies (Kennedy, 1982; Kennedy, 1983). These conditions often result in a loss of biotic diversity and a change in the ecological structure of planktonic and benthic communities, as well as damage to seagrass beds and coral reefs (National Research Council, 2000).

As the reduced form of inorganic nitrogen, ammonia enters coastal water bodies via numerous pathways and is also produced in bottom sediments by benthic organisms (Nedwell and Trimmer, 1996; Ryther and Dunstan, 1971; Trimmer et al., 1998). Historically, the largest source of ammonia to coastal water bodies was nitrogen-laden effluent from wastewater treatment plants.
Currently, sources of greater concern include agricultural runoff, industrial sources, and volatilization from wastewater treatment plants and large-scale farming operations (Asman et al., 1998; Sutton et al., 1995; Sutton et al., 2000). Less significant sources include mobile emissions and refrigeration facilities (Kean et al., 2000). Air emissions from these sources contribute to the direct and indirect atmospheric deposition of ammonia to coastal water bodies.

The study of the dry deposition of ammonia to coastal water bodies is a relatively new research concept that was once considered irrelevant by the scientific community (TBEP, 1996). However, over the last few decades, atmospheric scientists discovered that during dry conditions primary and secondary nitrogen species were settling through the airshed and depositing to water bodies (Hinga et al., 1991). Hicks et al. (2000) have shown that in some locations up to 40% of the nitrogen entering coastal water bodies followed the dry atmospheric deposition pathway.

Dry and wet deposition of ammonia and ammonium is a significant threat to coastal ecosystems because of their close proximity to source-rich regions. Because ammonia gas is highly water soluble, it has a relatively short atmospheric residence time of up to 10 days (Seinfeld and Pandis, 1998). Therefore most of the gaseous ammonia emitted locally is deposited to the land or water body that is located relatively close to the source. Research by Poor et al. (2001) discovered that in the Tampa Bay estuary, direct dry deposition of ammonia and wet deposition of ammonium were approximately 34% and 24% of the total (wet + dry) nitrogen deposition rate of 7.3 kg-N ha\(^{-1}\) yr\(^{-1}\), respectively.
Considering that an estimated 60% of the nitrogen that is directly deposited to Tampa Bay is in the form of either ammonia or ammonium, it was necessary to conduct further studies to gain a better understanding of this process.

This dissertation was structured as a compilation of independent research chapters with specific study objectives as follows:

➢ Chapter 2

• Determine the annual, seasonal, and diurnal concentrations of ammonia at an urban and rural monitoring site in the Tampa airshed;

• With regression modeling, determine if atmospheric ammonia concentrations at each site are affected by differing meteorological parameters;

• Discover if source trends exist between ammonia and its aerosol precursors.

➢ Chapter 3

• Characterize below-cloud scavenging of atmospheric ammonia during convective thunderstorms in the summer season;

• Utilize and validate a model to determine the relationship between below-cloud scavenging of ammonia gas and precipitation intensity;

• Investigate whether ammonium wet deposition causes a bi-directional ammonia flux in Tampa Bay during the summer season;

• Explore the effects of differing precipitation sampling techniques.
Chapter 4

- Verify the predictive ability of the NOAA Buoy model in the Tampa Bay estuary;
- Determine if the NOAA Buoy model accurately predicts over-water flux parameters when input measurements are made near-shore;
- If necessary, alter the model to increase accuracy;
- Calculate the flux of ammonia at the air/water interface and determine if Tampa Bay is a source or sink for atmospheric ammonia.

Chapter 5

- Discussion of conclusions and recommendations for future research.

The ultimate goal of this research endeavor is to provide to the local scientific community the knowledge necessary to develop effective nutrient management plans for ammonia in the Tampa Bay estuary.

1.2 The Tampa Bay Estuary

At 104,000 hectares, Tampa Bay is Florida’s largest open-water estuary and is divided into seven subunits: Old Tampa Bay, Hillsborough Bay, Middle Tampa Bay, Lower Tampa Bay, Boca Ciega Bay, Terra Ceia Bay, and the Manatee River (Lewis et al., 1988; Figure 1.1).
In a report published by the U.S. Department of the Interior, five bay management eras were proposed to describe the modern history of Tampa Bay. These periods ranged from an era of pristine natural conditions to the present era encompassing both the threat of irreversible damage to the bay as well as widespread public and private support for restoration and preservation of the
ecosystem (Lewis et al., 1988). As the bay evolves ecologically and commercially, it is necessary to refine our knowledge of efficient management schemes for continued protection and enhancement of the estuary.

1.2.1 Commercial Value

On an annual basis, Tampa Bay supplies billions of dollars to the region through tourism, trade, fishing, and development (TBEP, 1996). Located in Tampa Bay, the Port of Tampa is Florida’s largest port, controlling one-half of the seaport commerce that passes through the state and contributing 13 billion dollars to the local economy (Tampa Port Authority, 2003). While the Port of Tampa has historically handled the transfer of various goods including phosphorus, petroleum, and citrus products, it is also now home to several cruise lines that provide luxury vacations to both local residents and visitors.

In addition to trade, Tampa Bay is also home to the commercial and recreational fishing industries. The numerous indigenous fish and shellfish harvests are invaluable to the local economy. Species of interest include mullet, blue crabs, hard shell clams, tarpon, snook, and spotted seatrout (Lewis et al., 1988). Based on information from sport and commercial fishermen, the Tampa Bay Estuary Program estimates that fish populations are now in a state of flux, with populations of snook and red drum increasing, while mullet and spotted seatrout catches are at historical lows (TBEP, 1996). In fact, compared to 1950 harvests of 487,000 pounds, 1990 harvests of spotted seatrout have declined by 86% to 67,000 pounds (TBEP, 1996).
1.2.2 Ecological Value

The Tampa Bay estuary is home to a splendid community of flora and fauna that comprise the complex food chain of the bay. The following section provides an overview of this system so that one has an understanding of the estuary’s delicate ecological balance.

1.2.2.1 Algal Communities

Phytoplankton are characterized as free-floating, single-celled microscopic algae (Wolfe et al., 1990). As an important primary producer, phytoplankton are found throughout the bay and play an important role in the eutrophication process. In Tampa Bay, there are four main species including: phytomicroflagellates, diatoms, dinoflagellates, and blue-green algae, ranging in size from 5-um to 2-mm in diameter (Lewis et al., 1988).

Phytoplankton are an important food source for zooplankton and larval fish and form the food base for other animals in the estuary (Wolfe et al., 1990). In the upper reaches of Tampa Bay, blooms occur more frequently because of low flushing and mixing rates and increased nutrient addition (TBEP, 1996).

Benthic microalgae are similar in species to the phytoplankton, but instead of being suspended in the water column, microalgae live on the surfaces of rocks, seagrasses and sediment (Lewis et al., 1988). Although little is known about benthic microalgae, scientists suspect that they are an important food source for herbivores such as ciliates, small crustaceans and filter feeders, while providing stability to bottom sediments (Wolfe et al, 1990).
Macroalgae are defined as multicellular, macroscopic, photosynthetic algae that are usually found attached to a substrate such as seagrass blades, oyster shells, seawalls and docks and are believed to be an important source of food and shelter for benthic invertebrates (Wolfe et al., 1990). Drift algae is commonly seen in the bay and is believed to play a primary and secondary role in providing food to fish species, both by being directly consumed and as an attachment site for other algal forms that are also directly consumed (Lewis et al., 1988). However, similar to phytoplankton and microalgae, macroalgae are fueled by available nutrients, and are considered a nuisance species when in abundance, playing a role in the eutrophication of the bay (Wolfe et al., 1990).

1.2.2.2 Fauna

In Tampa Bay, zooplankton are present as holoplankton and meroplankton, with holoplankton spending their entire lives as plankton, and meroplankton spending only a portion of their lives as plankton, usually during the larval stage (Lewis et al., 1988). Examples of meroplankton include oysters, barnacles, pink shrimp, blue and stone crabs, and larval fish, which depend on holoplankton as a food source during this life stage (Lewis et al., 1988). Seagrasses play an important role in the survival of planktonic invertebrates by providing protection from predators (Zieman and Zieman, 1989).

Benthic invertebrates are animals that live at the sediment/water interface either by burrowing just below the surface or living on the surface of the sediment (Wolfe et al., 1990). As with other estuarine life forms, seagrasses provide food and shelter to these invertebrates with a direct correlation between seagrass
abundance and species diversity, and in the upper regions of the Tampa Bay estuary where water quality has been compromised, short-lived opportunist species dominate (Wolfe et al., 1990).

It is estimated that close to 200 fish species reside in Tampa Bay for either all or at least part of their lives (Wolfe et al., 1990). Tampa Bay is also an ideal nursery area for the larvae and juveniles of both resident and migratory species, due to the abundant food sources that are available to these species through the high productivity rate in the summer months (Lewis et al., 1988). In fact, spawning in the Gulf of Mexico and the resulting movement of these juveniles into Tampa Bay occurs during the summer season (Lewis et al., 1988).

Although numerous reptile species exist in the Tampa Bay watershed, only seven species are purely estuarine dependent, which include marine turtles, the mangrove water snake, and the diamondback terrapin (Wolfe et al., 1990). Because of the rapid development of the Tampa coastline, these species have experienced considerable decline due to habitat loss (TBEP, 1996).

There are only two mammalian species that reside in the Tampa Bay estuary, the Florida manatee and the bottlenosed dolphin. Due to seasonal water temperature variations, more manatees are found in the bay during the winter season, especially near the thermal discharge sites of local power plants (TBEP, 1996). Bottle-nosed dolphins are found evenly distributed throughout Tampa Bay and utilize mullet as their main food source (Wolfe et al., 1990).
1.2.2.3 Seagrass Ecosystems

The importance of seagrass habitats to the health and vitality of the Tampa Bay ecosystem cannot be overemphasized. Seagrasses are submerged flowering plants with roots and stems that live in the shallow waters of the estuary, and recognized as one of the most productive benthic habitats for the bay’s inhabitants (Zieman and Zieman, 1989). In addition to providing shelter, nursery, and feeding habitat for several fish and shellfish populations including snook, red drum, seatrout, shrimp, and bay scallops, they also provide food for the endangered Florida manatee, who are known to forage in the grass beds during the warmer months (TBEP, 1996). Seagrasses are utilized by sea turtles for food and shelter on a diurnal cycle, grazing the grass beds during the daytime and resting in nearby shoals during the evening hours (Zieman and Zieman, 1989). They also improve bay water quality by utilizing nutrients in the water column. Some species translocate ammonium and phosphate from the sediment through the root system, while others take in nutrients through the leaf structure (Lewis et al., 1988; Zieman and Zieman, 1989).

Five of the seven known seagrass species found in Florida’s waters are indigenous to Tampa Bay, which include: the turtle-grass, manatee-grass, shoal-grass, widgeon-grass, and star-grass (Lewis et al., 1988). The dominant species in the bay are the turtle-grass and shoal-grass, and based on current estimates, there are about 6,000 hectares of seagrass meadows in Tampa Bay (Wolfe et al., 1990). Considering that approximately 100 years ago it was estimated that
close to 30,000 hectares of seagrass meadows were present in Tampa Bay, significant losses have occurred over the past century (TBEP, 1996).

Between 1940 and 1963, many of the grass beds were filled in for waterfront development, while the remaining died off from the resulting siltation (Wolfe et al., 1990). Since 1963, the upper Tampa Bay regions have continued to experience losses, with Hillsborough Bay now devoid of all seagrass beds and Old Tampa Bay at a 60% reduction (Figure 1.2) (TBEP, 1996). The continued loss of seagrass beds was due mostly in part to reduced light penetration caused by increased turbidity from algae growth, which occurred when excess nutrients entered the bay from wastewater discharge and stormwater runoff (TBEP, 1996). However, lower segments of the bay have gained about 14% in areal coverage (Wolfe et al., 1990). The importance of seagrass beds to the health of the bay and their susceptibility to environmental contaminants make them an important indicator of Tampa Bay’s overall health (TBEP, 1996).
Figure 1.2 1950 and 1996 Seagrass Coverage (TBEP, 1996)
1.2.3 The Tampa Bay Estuary Program

The Tampa Bay Estuary Program (TBEP) was begun as a National Estuary Program in 1991. The purpose of the program was to assist the local community in the development of an estuarine management plan to restore Tampa Bay and protect it from the negative effects of significant population growth experienced in the area. The TBEP has formed a partnership between local governments and regulatory agencies, industries, academia, and community representatives to develop strategies to repair and protect the bay’s ecosystem in the most cost effective manner (TBEP, 1996). These partners have developed a set of action plans for bay improvement that address the following environmental needs (TBEP, 1996):

- Water and sediment quality
- Bay habitats
- Fish and wildlife
- Dredging and dredged material management
- Spill prevention and response
- Public education and involvement

A notable goal of the Water and Sediment Quality action plan is to cap nitrogen loadings at existing levels to encourage the regrowth of an additional 12,350 acres of seagrass, while preserving the bay’s existing seagrass beds (TBEP, 1996). A challenge to this goal will be the increased atmospheric deposition of nitrogen to the bay as a result of the influx of people to the region,
through additional automobile emissions, and the energy needs of a growing population.

1.3 Ammonia Impacts in a Coastal Estuary

1.3.1 Sources of Atmospheric Ammonia

Ammonia is a colorless gas with an odor threshold of approximately 25 ppm. It is the primary basic gas found in the troposphere and one of the most abundant nitrogen containing compounds (Seinfeld and Pandis, 1998). Both natural biological processes and anthropogenic sources emit ammonia to the atmosphere. The main biological source of ammonia in the troposphere is the microbial decomposition of organic waste materials, and less significant natural sources include oceanic, soil, fire, and plant emissions (National Research Council, 1979). Anthropogenic sources of ammonia contribute to elevated atmospheric concentrations of ammonia gas and ammonium aerosols. Examples of anthropogenic sources include:

- **Agricultural sources** - high-density animal housing, grazing, feedlot operations, manure storage and spreading, and synthetic fertilizer application.
- **Industrial sources** - fertilizer production, refineries, chemical processing plants, and strip mining.
➢ **Combustion processes** - municipal waste incineration, domestic heating, internal combustion engines, and power plants.

➢ **Miscellaneous sources** – food processing plants, human and animal excreta, large-scale refrigeration, and reprographics facilities.

Ammonia emissions have increased substantially since the 1950’s due to the increasing demands of a burgeoning human population and the resulting need for synthetic fertilizers for crop production. In the future, emissions are expected to continue to rise with the intensification of high-density livestock production techniques (Asman et al., 1998).

Global emissions of ammonia are estimated to be 54 Mt-N yr\(^{-1}\), with 60% of the emissions originating from anthropogenic sources (Asman et al., 1998). Ammonia emissions estimates in the United Kingdom are approximately 450-Gg (0.45 Mt) NH\(_3\) yr\(^{-1}\), with 90% of emissions attributed to agricultural activities (Sutton et al., 1995). A recent emission inventory found that in the United States, 90% of anthropogenic emissions originated from the combination of animal waste volatilization and fertilizer application (Goebes et al., 2003).

Ammonia emissions from agricultural sources vary seasonally and are based on agricultural practices and meteorological conditions. Emissions from animal housing and slurry ponds are positively correlated with ambient temperature and relative humidity, as ammonia volatilization increases with rising temperature and humidity (Genermont and Cellier, 1997). Therefore, higher ambient concentrations are found in the spring and summer months in North
America (Asman et al., 1998). Likewise, atmospheric turbulence and unstable conditions result in increased transport of ammonia from source-rich regions.

The most optimal conditions for ammonia volatilization and transport from agricultural sources occur during afternoon hours in the summer season. Ammonia emissions in high-density urban areas are more evenly distributed among sources but may exhibit diurnal fluctuations related to traffic patterns, because the bulk of emissions originate from mobile and other point sources. Battye et al. (2003) found that agricultural sources accounted for the bulk of ammonia emissions in both North Carolina and the San Joaquin Valley of California, with livestock waste and fertilizer application contributing approximately 86% and 70%, respectively. However, in the Charlotte, NC, and Fresno, CA urban areas, the distribution of emissions is more heavily weighted toward automobile emissions, with highway vehicles contributing 64% of emissions in Charlotte and 51% of emissions in Fresno. The disparity is even greater in the winter for both urban areas, with agricultural emissions declining to only 14%, increasing the relative contribution of vehicle emissions during the winter season (Battye et al., 2003).

1.3.2 Tampa Bay Emissions Inventory

In 2001, an ammonia emissions inventory was developed for the Tampa region (Mizak, 2001). The inventory included data for Hillsborough, Pinellas, and Polk counties and the results used in conjunction with atmospheric modeling studies conducted for the region. Because ammonia is not a Clean Air Act
regulated pollutant, data from three sources was used to build the inventory as follows:

- 1999 EPA Toxics Release Inventory (TRI)
- Section 302 Emergency Planning and Community Right to Know Act (EPCRA) Legislation
- Carnegie Mellon University - Ammonia Emissions Inventory Program

1.3.2.1 1999 TRI

The Toxics Release Inventory is a database containing information about more than 650 toxic chemicals that are being used, manufactured, treated, transported, or released into the environment. Manufacturers are required to report the locations and quantities of chemicals stored on site to state and local governments. Facility information includes air emissions, surface water discharges, releases to land, underground injections, and transfers to off-site locations (US EPA, 2002) (http://www.epa.gov/enviro/html/toxic_releases.html).

1.3.2.2 Section 302 EPCRA Legislation

Facilities possessing ammonia in excess of 500 pounds, the Threshold Planning Quantity (TPQ) for NH$_3$, must file annual reports in accordance with Section 312 of the Legislation, a detailed inventory of reportable substances on the “Tier Two Form”. Information is reported to the State Emergency Response Commission (SERC), which is responsible for implementing EPCRA provisions within each state and the Local Emergency Planning Committee (LEPC) (http://www.yosemite.epa.gov/oswer/CeppoWeb.nsf/content/epcraoverview.html).
1.3.2.3 CMU Ammonia Emissions Inventory Program

Researchers at Carnegie Mellon University developed an ammonia emissions inventory computer program consisting of input and output data files, and an executable program. The program utilized default data from 1999 as input files to calculate ammonia emissions on a county, state, or national scale, which are provided as user specified output files. The input data files consist of several text files containing the latest ammonia emission factors, activity data by category, and county information (Strader et al., 2001). Default data was utilized for analysis in the Tampa region. The inventory program is available at http://www.envinst.cmu.edu/nh3/.

1.3.2.4 Results

Based on data compiled from the three aforementioned sources, 2001 ammonia emissions for the three counties totaled approximately 15,900 tons yr\(^{-1}\) (Table 1.1; Figure 1.3). Polk County contributed 55% of the emissions, with Hillsborough and Pinellas counties contributing 35% and 10%, respectively. The majority of Polk County’s emissions were from livestock, fertilizer, and point sources (84%). Hillsborough County’s emissions were dominated by livestock and fertilizer sources (62%). Humans and domestic animals made up 18% of ammonia emissions while point sources comprised approximately 8% of emissions in the county. Pinellas County is one of the most densely populated and urbanized counties in the state of Florida. Emissions from humans and domestic animals constituted 58% of the county’s ammonia emissions. Livestock and fertilizer sources comprised 27% of the remaining emissions.
Due to the geography of the Tampa region, the majority of local sources are located to the east of the bay. Therefore one would expect to find increased atmospheric ammonia and ammonium concentrations over the bay when the prevailing winds are from the east/northeast/southeast directions (Figure 1.1).
Table 1.1 Annual Ammonia Emissions in Polk, Hillsborough, and Pinellas Counties

<table>
<thead>
<tr>
<th>Source</th>
<th>Polk</th>
<th>Hillsborough</th>
<th>Pinellas</th>
<th>Total (2001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Categories</td>
<td></td>
<td></td>
<td></td>
<td>(tons yr⁻¹)</td>
</tr>
<tr>
<td>Point</td>
<td>2837</td>
<td>422</td>
<td>1</td>
<td>3260</td>
</tr>
<tr>
<td>Livestock</td>
<td>3392</td>
<td>2728</td>
<td>214</td>
<td>6334</td>
</tr>
<tr>
<td>Fertilizer</td>
<td>1062</td>
<td>698</td>
<td>235</td>
<td>1995</td>
</tr>
<tr>
<td>Soil</td>
<td>628</td>
<td>333</td>
<td>93</td>
<td>1054</td>
</tr>
<tr>
<td>POTW</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Humans</td>
<td>210</td>
<td>462</td>
<td>437</td>
<td>1109</td>
</tr>
<tr>
<td>Domestic Animals</td>
<td>265</td>
<td>539</td>
<td>518</td>
<td>1322</td>
</tr>
<tr>
<td>Wild Animals</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Fire</td>
<td>11</td>
<td>6</td>
<td>2</td>
<td>19</td>
</tr>
<tr>
<td>Mobile</td>
<td>89</td>
<td>171</td>
<td>125</td>
<td>385</td>
</tr>
<tr>
<td>Other</td>
<td>217</td>
<td>154</td>
<td>34</td>
<td>405</td>
</tr>
<tr>
<td><strong>Total (tons yr⁻¹)</strong></td>
<td><strong>8713</strong></td>
<td><strong>5515</strong></td>
<td><strong>1660</strong></td>
<td><strong>15888</strong></td>
</tr>
</tbody>
</table>

Figure 1.3 Annual Ammonia Emissions in Polk, Hillsborough, and Pinellas Counties
1.3.3 Ecological Impacts

1.3.3.1 Atmospheric Transport and Deposition

Atmospheric ammonia, the most abundant alkaline component in the atmosphere, is emitted initially in the gaseous form (NH₃). Once emitted, some of the ammonia gas will neutralize the oxidation products of sulfur dioxide (SO₂) and nitrogen oxides (NOₓ) to form ammonium sulfate and bisulfate and ammonium nitrate according to the following reactions (Seinfeld and Pandis, 1998):

\[ \text{NH}_3(g) + \text{H}_2\text{SO}_4(g) \leftrightarrow \text{NH}_4\text{HSO}_4(s) \]  
\[ \text{NH}_4\text{HSO}_4(s) + \text{NH}_3(g) \leftrightarrow (\text{NH}_4)_2\text{SO}_4(s) \]  
\[ \text{NH}_3(g) + \text{HNO}_3(g) \leftrightarrow \text{NH}_4\text{NO}_3(s) \]

At the Gandy Bridge site, 1-year (2002-2003) of research results show that there exists an “ammonia-poor” environment, with an average molar ratio of total ammonia to sulfate equal to approximately 0.8. This occurs when there is insufficient ammonia to neutralize the available sulfate and is determined when the molar ratio of total ammonia to total sulfate is less than 2 (Seinfeld and Pandis, 1998). These conditions prevent the formation of the unstable ammonium nitrate compound as all of the available ammonia preferentially reacts first with sulfate.
Ammonia and ammonium are removed from the atmosphere by dry and wet deposition processes (Figure 1.4). Dry deposition occurs when gaseous and particulate species are removed from the atmosphere onto surfaces in the absence of precipitation (Seinfeld and Pandis, 1998). The dry deposition of ammonia occurs relatively close to its source, but dry deposition of the ammonium aerosol occurs further downwind from the source, due to its low deposition velocity (Sutton et al., 1998). Asman (1998) utilized a model to calculate the dry deposition of ammonia gas as a function of the downwind distance from a source. Results of the study showed that approximately 60% of the ammonia emitted at a 3-m elevation deposited 2000-m from the source. These results clearly illustrate that ammonia is deposited close to a source due to the typical low source height and small surface resistance characteristics of area source emissions.

The difference between the gas and particulate species’ dry deposition characteristics lies in their atmospheric residence times. Ammonia has a relatively short atmospheric residence time due to its small surface resistance and high solubility in water (Seinfeld and Pandis, 1998). Conversely, the ammonium aerosol has a longer residence time because of its small size (~0.5 µm diameter) and corresponding low deposition velocity. Ammonium aerosols can also be transported long distances if captured in the upper winds of the troposphere.

Wet deposition occurs when gases and aerosols are scavenged by rain, snow, clouds, and fog and transported to the surface of the Earth (Seinfeld and
Pandis, 1998). During a precipitation event, the droplets scavenge ammonia and ammonium. Ammonia gas reacts with the water molecules to form the ammonium ion:

$$\text{NH}_3(\text{g}) + \text{H}_2\text{O(aq)} \leftrightarrow \text{NH}_4^+(\text{aq}) + \text{OH}^-$$  

(Equation 1.4)

The equilibrium constant ($K$) for Equation 1.4 at standard temperature is $1.7 \times 10^{-5}$ M (Seinfeld and Pandis, 1998). At pH values lower than 8, most of the dissolved ammonia is in the form of the ammonium ion.

Wet deposition trends are more spatially distributed throughout a region, due to the rapid mixing of aerosol particles in the troposphere. However, dry deposition of ammonia gas exhibits large concentration gradients with highest concentrations found near a source-rich region.

Figure 1.4 Atmospheric Transport and Deposition Processes (Pew Oceans Commission, 2001)
1.3.3.2 Ecological Effects of Ammonia

Because nitrogen is the limiting factor in algal growth in most coastal estuaries, excessive inputs of ammonia-nitrogen to a coastal water body can lead to eutrophic conditions. Eutrophication results from unhealthy increases in the rate of photosynthetic primary production or phytoplankton growth. Ammonia inputs are now of great concern because it is the preferred nitrogen source of phytoplankton, as it is easily assimilated during their life cycle (Day et al., 1989).

Primary sources of ammonia within the estuarine system include benthic regeneration, tidal exchange, and nitrogen fixation (National Research Council, 1979). The typical vertical distribution of ammonia in the water column of an estuary follows a pattern of increasing concentration with depth (National Research Council, 1979). However, when external sources constantly supply excessive amounts of ammonia to the system, high levels of ammonia are found throughout the water column (Day et al., 1989).

Ammonia in marine sediments is formed by the bacterial decomposition of organic materials and due to large concentration gradients, is transported into the overlying waters by molecular diffusion (Day et al., 1989). Under typical conditions, seagrasses and microrganisms present at the interface of the sediment and water will utilize the ammonia, thereby reducing the amount of ammonia available to phytoplankton in the water column (National Research Council, 2000). However, when large amounts of ammonia are delivered to the surface of a water body by external sources, increasing phytoplankton biomass often results in algal blooms.
The effects of eutrophication on a coastal ecosystem can be severe. Increased productivity often results in hypoxic (low-oxygen) or anoxic (oxygen-free) conditions, which lead to fish kills if acute, or subtle changes in ecosystem decline leading to more pronounced long term biological changes if chronic (Cloern, 1996) (Figure 1.5).

**Figure 1.5 An Illustration of Eutrophication (Pew Oceans Commission, 2001)**

Particularly vulnerable to damage from eutrophication or nutrient over-enrichment are seagrass beds (National Research Council, 2000; TBEP, 1996; Zieman and Zieman, 1989). Like phytoplankton, macroalgae are fueled by excess nutrients. When phytoplankton biomass and total suspended solids
increase, macroalgae become more abundant on seagrass leaves, contributing to light attenuation and reduced gas and nutrient exchange and eventually leading to seagrass decline and displacement (National Research Council, 2000). Considering it is now estimated that at least half of all estuaries in the United States are experiencing some form of eutrophication, it is necessary to determine if increased ammonia inputs are a contributing factor.

Estuaries, shallow coastal waters and continental shelf waters cover only 15% of the world’s ocean area, but account for nearly half of the oceanic primary production of phytoplankton. This disproportionality is attributed in part to anthropogenic nitrogen loading from the atmosphere (Paerl, 1997). In a related study, Paerl and Whitall (1999) conducted research in the North Atlantic Ocean and discovered that increases in anthropogenically enhanced atmospheric ammonia deposition are linked to increases in harmful algal blooms along the coastline of the North Atlantic Basin.

1.4 Total Maximum Daily Load (TMDL) Regulations

The total maximum daily load requirement was first described in section 303(d) of the Clean Water Act. However, the TMDL rule was not published until 1985, and then amended in 1992 (Total Maximum Daily Load Program, 1985). TMDLs establish the maximum amount of a pollutant that a water body can take in without causing impairment. The original intent of the requirement was to establish maximum daily loads for pollutants in surface waters that were exceeding applicable water quality standards (US EPA, 1972). The states are
responsible for identifying and priority ranking these impaired waters and must consider seasonal variations and a margin of safety for insufficient knowledge of the relationship between sources and water quality. The development of priority rankings for segments of a water body are based on the severity of the pollution and the pollutants causing the impairment, as well as the uses for the waters. The establishment of TMDLs may be made on a pollutant-by-pollutant basis or by utilizing a biomonitoring approach, or both. Beginning in 1992 and continuing biennially, each state is required to submit to the U.S. Environmental Protection Agency for approval, a list of waters, pollutants causing impairment, and a priority ranking including waters targeted for TMDL development within the following two years (Total Maximum Daily Loads, 1985).

In 1999, the State of Florida published the Florida Watershed Restoration Act, which outlined the implementation of water quality standards and the TMDL program. The act defined the total maximum daily load as “the sum of the individual wasteload allocations for point sources and the load allocations for nonpoint sources and natural background” (Florida Department of Environmental Protection, 1999). The act also designates the Florida Department of Environmental Protection as the lead agency in administering the program and requires collaboration with local governments, water management districts, the Department of Agriculture and Consumer Services, environmental groups, regulated interests, other state agencies, academic institutions, and affected pollution sources. The Florida Watershed Management Program is based on a
five-phase cycle that rotates through Florida’s basins every five years. The phases are as follows:

- Initial Basin Assessment
- Coordinated Monitoring
- Data Analysis and TMDL Development
- Basin Management Plan Development
- Implementation of Basin Management Plan

In June 1998, a total nitrogen TMDL for Tampa Bay was approved and established by the U.S. Environmental Protection Agency. For purposes of the program, Tampa Bay proper (ID# 1558) was divided into seven segments (C, D, E, F, G, H, and I) (Figure 1.6). The three segments with high nitrogen loadings and maximum impact included: 1558E (Upper Hillsborough Bay), 1558H (Old Tampa Bay) and 1558I (Old Tampa Bay) (US EPA, 1998). The Florida Watershed Restoration Act has since superceded the Tampa Bay TMDL and the Florida Department of Environmental Protection is currently in the process of reviewing the year 2003 draft TMDL for Tampa Bay.

Beginning in 2001, a collaborative effort between EPA’s Office of Air and Radiation and the Office of Water was initiated. This partnership was formed to assess and reduce the atmospheric deposition of toxics and nitrogen to all waterbodies in the United States, and was borne out of the need for a more comprehensive understanding of the relationship between atmospheric deposition of pollutants and their effects on sensitive ecosystems. Under the authorities of the Clean Air Act and Clean Water Act, a work plan was developed
with a schedule of specific activities. An important component of this work plan is a collaboration with the states that supports the development and implementation of atmospheric deposition focused TMDLs (US EPA, 2001).

In coastal ecosystems, the TMDL approach is now widely considered an important management tool for the determination of desired outcomes and the nutrient load reductions needed to attain them (Boesch, 2002). The research results presented in this dissertation can be utilized by local and state regulators for the development of a TMDL for ammonia. This information can also play an integral role in the development of a TMDL for air sources of total nitrogen.
Figure 1.6 Section 303(d) Listed Water Segments in Hillsborough County (Florida Department of Environmental Protection, 1999)
1.5 Research Site Descriptions

NH$_x$ (NH$_3$ + NH$_4^+$) and meteorological sampling was conducted over a 2-year period at four monitoring sites, with nutrient sampling conducted at the Gandy Bridge site since 1996 (Figure 1.7). Each site is described as follows (Figures 1.8 - 1.11):

- **Gandy Bridge** - The Gandy Bridge monitoring site is located at the eastern end of the Gandy Bridge adjacent to Old Tampa Bay at Latitude 27N 53’ 33”, Longitude 82W 32’ 15”. The site has been operational for atmospheric deposition monitoring since 1996. Due to its location in Tampa, this site represents an urban environment. In addition to the 1-in-6 day sampling for ammonia and ammonium, daily integrated sampling was conducted at the site along the seawall during the Summer 2003 season.

- **Picnic Island** - This site is located at Latitude 27N 51’ 46”, Longitude 82W 33’ 16”, in an industrialized area of Tampa called Old Port Tampa. Picnic Island Park is maintained and operated by the City of Tampa as a recreational park. Daily, integrated sampling was conducted on a 46-m fishing pier for two, 2-week periods in November 2002 and January 2003.

- **Sydney** - The Sydney monitoring site became operational in Spring 2002 for the Bay Regional Atmospheric Chemistry Experiment (BRACE) research study. During May 2002, intensive sampling occurred daily. From June 2002 to May 2003, sampling occurred
on a 1-in-6 day schedule. Sydney is sited east of Tampa in a rural location at Latitude 27N 57' 56", Longitude 82W 13' 56".

Port Manatee Turn - A tower located in Middle Tampa Bay housing meteorological and oceanographic sensors to measure the turbulent fluxes of atmospheric constituents across the air/water interface. The tower is located at Latitude 27N 39' 50", Longitude 82W 34' 50", approximately 7 nautical miles southeast of St. Petersburg, FL, and 4 nautical miles west-northwest of Port Manatee, FL. The tower is in approximately 5-m water depth and extends 10-m above the water surface.
Figure 1.7 Tampa Research Sites
Figure 1.8 Gandy Bridge

Figure 1.9 Picnic Island
Figure 1.10 Sydney

Figure 1.11 Port Manatee Turn Tower
CHAPTER 2
ATMOSPHERIC AMMONIA CHARACTERISTICS IN AN URBAN AND RURAL SETTING

2.1 Introduction

Tampa Bay, like other large estuaries and sensitive ecosystems in the United States and abroad, has experienced considerable decline due to nutrient enrichment. Examples of similarly affected ecosystems include the Chesapeake Bay estuary in Maryland, the Neuse River ecosystem in North Carolina, and locations throughout Western Europe. To elucidate the role that atmospheric ammonia plays in the decline and degradation of an ecosystem, studies have been completed detailing the spatial and temporal characteristics of ammonia in both urban and rural settings.

On a seasonal basis, ambient ammonia concentrations would be expected to escalate with temperature, due to increased volatilization from area sources. A 2-year study was conducted in the Chesapeake Bay estuary to determine ammonia and ammonium concentrations at both an urban and a rural site (Larsen et al., 2001). Results indicated that concentrations at the rural site varied by season with the highest concentrations found during the summer and lowest during the winter. However, there was no seasonal signal detected at the urban site because the local mobile emissions overpowered the seasonal
background. Robarge et al. (2002) conducted one year of 12-hour ammonia and ammonium measurements at a rural site in the Neuse River watershed and found a large disparity in seasonal concentrations. In fact, based on statistical analysis of their dataset (n~600), they determined that the ammonia concentration increased exponentially with temperature, which explained 54% of the variation in the data. Low variability was observed diurnally, with daytime measurements only slightly higher than nighttime concentrations. More recently, a study conducted by Walker et al. (2004) in the Coastal Plain region of North Carolina found that ammonia concentrations are positively correlated with county emission densities and highest during the summer season. Diurnally, concentrations were higher during both the daytime and nighttime depending on the location in relation to local emission densities. Ammonium concentrations were diurnally consistent although seasonal concentrations were highest during the winter at all sites.

Studies conducted in Europe provided similar results. Ammonia measurements made in rural locations in Scotland show a seasonal relationship between temperature and ambient concentration (Burkhardt et al., 1998; Fowler et al., 1998). During the winter months, the average ambient ammonia concentrations decreased by approximately 50% and the highest average ambient ammonia concentrations occurred during the summer months, with only a few exceptions (Fowler et al., 1998). The site was located in close proximity to a field that utilized slurry spreading as a fertilization method, therefore large
peaks in ambient concentrations occurred in the spring and fall seasons when this practice took place, skewing the seasonal data (Burkhardt et al., 1998).

Researchers in Rome, Italy studied the patterns of ambient ammonia concentrations between an urban site located near a busy traffic intersection, an urban background site, and a rural site. Concentrations at the traffic site were consistently five times greater than those at the urban background site and always higher than rural concentrations. In addition, air temperature was a key variable at the rural site but elevated winter concentrations at the urban locations indicated that mobile source emissions affected concentrations in the urban environment even more than temperature (Perrino et al., 2002).

Source location and proximity measured through wind speed and direction also contribute to elevated ammonia concentrations. Results of a Denmark study measuring ammonia deposition to a spruce forest showed peak ambient concentrations under stable atmospheric conditions and when winds were from a local source-rich region (Anderson et al., 2003). In Scotland, measured ammonia concentrations peaked when wind speed and direction were greater than 1 m s\(^{-1}\) and from a direction where several farms were located (Burkhardt et al., 1998). A regression model was utilized in North Carolina to explain the variation in ammonia concentrations. Temperature, wind speed and direction explained 76% of the variation in the 12-hour mean concentrations, indicating that local agricultural sources significantly affected ammonia concentrations in this region (Robarge et al., 2002).
2.2 Objectives and Hypotheses

The objectives of this research were to elucidate the annual, seasonal, and diurnal trends in ambient ammonia and ammonium concentrations at the urban Gandy Bridge and rural Sydney monitoring sites in Tampa. The following research questions and hypotheses will be addressed in this chapter:

➢ What are the spatiotemporal distributions of ammonia and ammonium in the Tampa Bay region?
  - Hypothesis 1: Maxima and minima concentrations will occur in the summer and winter seasons, respectively.
  - Hypothesis 2: Elevated ammonia concentrations will occur in the evenings when prevailing winds are low.
  - Hypothesis 3: Ambient concentrations will vary spatially in the region based on proximity to local sources.

➢ Are ammonia and ammonium concentrations affected by meteorological parameters at both the urban and rural sites?
  - Hypothesis 4: Ambient concentrations will increase with increasing temperature and when winds are from a source-rich region.

2.3 Study Locations and Duration

Gaseous ammonia and aerosol ammonium sampling was conducted at the Gandy Bridge and Sydney sampling sites. Data from the Gandy Bridge site was collected for 24-hours every 6 days beginning in January 1997 and ending
May 2003, a sampling schedule consistent with the US EPA National Ambient Monitoring System (NAMS) schedule for particulate matter (Poor et al., 2001). However, during May 2002, daily, integrated 12-hour measurements were made at the Gandy Bridge site. Sydney sampling began in May 2002 and 12-hour measurements occurred daily for that month. Beginning June 2002, sampling occurred according to the NAMS 24-hour 6-day schedule through May 2003 at Sydney.

2.4 Sample Collection and Analysis

Ambient air concentrations of gaseous ammonia and aerosol ammonium were obtained using URG Inc., annular denuder systems (ADS) as described by Vossler et al. (1998) and Poor et al. (2001). This method is similar to that described in Compendium Method IO-4.2 titled, “Determination of Reactive Acidic and Basic Gases and Strong Acidity of Atmospheric Fine Particles” (US EPA, 1999). The ADS at the Gandy Bridge and the sequential ADS at the Sydney site operated at an airflow of 10 L min\(^{-1}\) and 16.6 L min\(^{-1}\), respectively. The Gandy Bridge and Sydney sequential ADS were housed in fan-cooled boxes with inlet heights of 4.2-m and 2-m, respectively.

As described by Poor et al. (2001), each ADS consisted of a 2.5-µm particle aerodynamic diameter cut-point Teflon coated cyclone inlet, a 150-mm long gas denuder coated with either citric acid (C\(_6\)H\(_8\)O\(_7\)) (1996 to 2002) or phosphoric acid (H\(_3\)PO\(_4\)) (2002 to 2003) (1% w/v) in an 80% v/v methanol solution to absorb ammonia, and a filter pack in series (Allegrini et al., 1987).
The denuder coating solution was changed from citric acid to phosphoric acid after McCulloch and Shrendikar (2000) found that phosphoric acid coated denuders afford a stronger bond strength with ammonia. A single 47-mm diameter nylon filter collected ammonium aerosols. As determined by Allegrini et al. (1987) and Perrino et al. (2001), the denuder collection efficiency for ammonia was greater than 99%.

From 1996 through 2001 at the Gandy Bridge site, Harding ESE, Inc. (Gainesville, FL) prepared, extracted, and analyzed the denuders and filters, while technicians from the Environmental Protection Commission of Hillsborough County (EPCHC) operated the annular denuder systems. Samples were analyzed for ammonia and ammonium by automated colorimetry.

From 2002 to 2003 at the Gandy Bridge and Sydney sites, the University of South Florida (USF), College of Public Health Environmental Laboratory prepared, extracted, and analyzed the denuders and filters. The denuder and filter extracts were analyzed for ammonium using a Dionex DX-600 ion chromatograph with a CS12G guard and a CS12A analytical column. All samples were stored in 10-ml Dionex vials and refrigerated until analysis.

Denuders were prepared in the laboratory by first rinsing with a steady stream of >18 M\(\Omega\) deionized water for 1 minute. Approximately 5-ml of coating solution were added and the denuder shaken for 10 seconds. The 5-ml were drained and the denuder was again filled with the coating solution so that the glass on the flow-straightening end was covered. The denuder was placed on a spinner for approximately 10 minutes, drained, and dried with zero air (Vossler et
al., 1988). After sample collection and upon return to the laboratory, 10-ml of >18 MΩ deionized water was added and the denuder placed on the spinner for approximately 10 minutes to remove the collected ammonia. The extract was then decanted into a Dionex autosampler vial for IC analysis.

Filter packs were prepared by first disassembling the filter pack and placing a clean stainless steel screen in the filter ring housing. Using clean stainless steel forceps, a 47-mm diameter nylon filter was placed over the screen and then the large outer sleeve was screwed onto the filter base. The filter pack was then secured to the denuder. Filters were extracted by removing the nylon filter with clean forceps, placing in a 15-ml centrifuge tube, adding 10-ml of >18 MΩ deionized water and sonicating for 30 minutes (Vossler et al., 1988). The filter extract was decanted into a Dionex autosampler vial for IC analysis.

In addition to gas and aerosol measurements, meteorological parameters were continuously measured at the two sites. Measured parameters included air temperature, relative humidity, wind speed, and wind direction (Table 2.1).

| Table 2.1 Meteorological Data Collected at the Gandy Bridge and Sydney Sampling Sites |
|-----------------------------------------------|-----------------------------------------------|
|                                | Gandy Bridge | Sydney | Gandy Bridge | Sydney |
| Air Temperature                | 6            | 10     | Hour         | Minute |
| Relative Humidity              | 6            | 10     | Hour         | Minute |
| Wind Speed                     | 10           | 10     | Minute       | Minute |
| Wind Direction                 | 10           | 10     | Minute       | Minute |
2.5 Quality Assurance/Quality Control

Denuders and filter packs were washed thoroughly with >18 MΩ deionized water. Denuders were then soaked with >18 MΩ deionized water and the filter packs were dried and stored in a covered bin for further use.

Assembled denuders and filters were marked with factory installed identification numbers and lab technicians affixed unique labels identifying the run date and time prior to each operation. These labels were then transferred to Dionex vials upon extraction of the denuders and filters. Field logs stored at the sampling sites were initialed by the attending operator who recorded the identification numbers, sampling dates, on and off times, flow rates, elapsed time, and pass or failure status of leak tests. Leak tests were performed every time an assembled denuder was installed for operation to insure that the ADS did not contain leaks that would decrease airflow through the assembly. ADS flow rates were calibrated annually by EPCHC technicians, unless a problem was noted with the daily flow check. Airflow was mass-controlled within 2% of the set flow rate (URG, 1996).

Laboratory blanks were conducted every time denuders were processed to diagnose methodological problems. Several field blanks were conducted to determine operational problems. Both laboratory and field blanks were typically a factor of 10 or more below the sample concentrations. During IC analysis, ammonium check standards were run every 10 samples and at the beginning and end of each sequence. Additionally, for every 10 samples, one of the
samples was injected twice as a measure of reproducibility. Standards were within 10% of the set concentrations and reproducibility of the duplicates was within 3%. Water was also injected every 10 samples to check for carryover.

Total uncertainty was determined using paired field observations (n=315) from January 1997 through April 2003 at the Gandy Bridge site. For ammonia and ammonium, the total relative precision was 15% and 20%, respectively (Poor et al., 2002). To determine if there was a bias between the sampling inlet heights at Gandy Bridge and Sydney, respectively, simultaneous 24-hour integrated measurements of ammonia and ammonium were made at 5-m and 2-m for four days at the Gandy Bridge site. The total relative precision for ammonia and ammonium was 13% and 9%, respectively. This indicates that there was no bias in the sampling caused by the difference in inlet heights.

An absorption efficiency study was also conducted at the Gandy Bridge site to determine if reduced collection efficiency is a source of bias in the ADS measurements at sampling flow rates greater than 10 L min⁻¹. Collocated 24-hour integrated measurements were made for four days at a flow rate of 20 L min⁻¹, resulting in a denuder absorption efficiency and relative precision of 96% and 16%, respectively. These results indicate that there is an insignificant loss of ammonia from the coating layer of the denuder. In addition, the relative precision for ammonia at 20 L min⁻¹ was not significantly different from the previously determined value of 15% for a flow rate of 10 L min⁻¹.

Box plots are used to display the annual, seasonal and diurnal data. The boundary of the box closest to zero indicates the 25th percentile, a line within the
box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers below and above the box indicate the 10th and 90th percentiles, respectively (SPSS Inc., 1986).

2.6 Statistical Analysis

Unpaired, two-sided t-test analysis, at the 95% confidence level, was utilized to determine if there was a statistically significant difference between the annual, seasonal, and diurnal ammonia and ammonium concentrations at the Gandy Bridge and Sydney monitoring sites. The analyses were conducted using the data analysis tool in Microsoft Excel®.

Principal component analysis (PCA) is a data reduction technique that linearly transforms a large set of variables into a substantially smaller set of uncorrelated variables that represent most of the information in the original dataset (Dunteman, 1989). This technique was used in this study to determine the meteorological parameter(s) that most influence ammonia concentrations at the sampling sites. Multiple linear regression analysis was also utilized to determine the parameters that represent the variation in ambient ammonia concentrations at the Gandy Bridge and Sydney sites. PCA and regression statistics were calculated using SYSTAT® software.

To improve accuracy during statistical analysis of the data, ammonia and ammonium concentrations were log-transformed to improve fit, since concentrations follow a log-normal distribution (Figures 2.1 and 2.2).
Figure 2.1 Histogram of 24-hour Average Ammonia Concentrations at Gandy Bridge (n=315)

Figure 2.2 Histogram of 24-hour Average Ammonium Concentrations at Gandy Bridge (n=315)
2.7 Results and Discussion

2.7.1 Annual Averages

Annual average ammonia and ammonium concentrations at the Gandy Bridge site (1997-2003; n=315) were \(1.59 \pm 1.14\) and \(0.86 \pm 0.71\) \(\mu\)g m\(^{-3}\) (\(~2.45\) \(\mu\)g m\(^{-3}\) total ammonia), respectively. Concentrations at the Sydney site (2002-2003; n=53) were \(1.59 \pm 0.98\) and \(0.59 \pm 0.52\) \(\mu\)g m\(^{-3}\) (\(~2.18\) \(\mu\)g m\(^{-3}\) total ammonia), respectively (Figures 2.3 and 2.4; Table 2.2). These concentrations are comparable with those found in the Chesapeake Bay estuary, an ecosystem also experiencing eutrophic conditions and located near a growing urban area. Total ammonia concentrations (\(NH_x=NH_3+NH_4^+\)) at an urban site in Baltimore, MD and rural site in Solomons, MD were \(2.7 \pm 1.7\) and \(1.0 \pm 0.8\) \(\mu\)g m\(^{-3}\), respectively (Larsen et al., 2001). The Tampa concentrations are also comparable with those found for a low emission density site located in North Carolina’s Coastal Plain region at \(2.46\) \(\mu\)g m\(^{-3}\) but lower than those found at a site affected by a high emission density agricultural area at \(5.30\) \(\mu\)g m\(^{-3}\) (Walker et al., 2004). In a low ammonia emission agricultural region of the Netherlands, Buijsman et al. (1998) measured ambient ammonia concentrations at approximately \(3\) \(\mu\)g m\(^{-3}\). Matsumoto and Okita (1998) measured ammonia and ammonium concentrations in Nara, Japan, a medium-sized city comparable to Tampa. Average ammonia and ammonium concentrations in this city were \(2.43\) and \(1.70\) \(\mu\)g m\(^{-3}\), respectively, which is higher than the concentrations found at the Tampa sites, but within the statistical range. Urban ammonia concentrations
during the summer in Pittsburg, PA and Vinton, VA were in the range of 0.38 to 1.49 $\mu$g m$^{-3}$ (Leaderer et al., 1999; McCurdy et al., 1999).

Concentrations in pristine locations, far from agricultural sources, are considerably lower and represent background conditions. Air samples collected above Niwot Ridge, a pristine mountain range in Colorado, had ammonia and ammonium concentrations of 19.8 and 42.1 ng m$^{-3}$ (Rattray and Sievering, 2001), almost two orders of magnitude lower than those found in the Tampa Bay estuary. Conversely, ammonia concentrations at a high-traffic site in Rome, Italy ranged from 13.5 to 21.6 $\mu$g m$^{-3}$, exhibiting the effects of ammonia emissions from catalytic converters (Perrino et al., 2002).

It is peculiar that the average annual ammonia concentrations at the Gandy Bridge and Sydney sites are almost equal in value and are not statistically different ($p=0.55$). Considering that the Gandy Bridge and Sydney sites are located in urban and rural settings, respectively, the Gandy Bridge site would be expected to have higher average concentrations than the Sydney site (Larsen et al., 2001; Perrino et al., 2002). However, because both sites are most likely influenced by different source types, it is not unreasonable to find similar ambient concentrations.

Average annual ammonium concentrations were found to be statistically different at the two sites ($p=0.0002$), with the concentration at Gandy Bridge almost 50% greater than the Sydney site. It was determined that at Gandy Bridge, higher concentrations of sulfur dioxide are present, favoring the formation
of ammonium bisulfate. Therefore, it is not unreasonable for Gandy Bridge to have higher ambient ammonium concentrations than Sydney.

In Figure 2.5 is shown the fraction of ammonia in the gas phase, which exceeds 0.5 at both sites. A higher fraction of ammonia is in the gas phase at the Sydney site than at Gandy Bridge, indicating that Sydney is likely more strongly influenced by local ammonia emissions, while at Gandy Bridge aerosol formation is dominant.
Figure 2.5 Annual Ratio of NH₃ to NH₃+NH₄⁺

![Bar chart showing the annual ratio of NH₃ to NH₃+NH₄⁺ for Gandy Bridge and Sydney.]

Table 2.2 Annual Summary Statistics of 24-hour Average NH₃ and NH₄⁺ Concentrations (µg m⁻³)

<table>
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<th>Location</th>
<th>NH₃</th>
<th>NH₄⁺</th>
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<th>Median</th>
<th>SD</th>
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<td>1.14</td>
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<td>0.98</td>
<td>0.52</td>
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2.7.2 Seasonal Variations

In general, seasonal ammonia concentrations did not vary significantly at Gandy Bridge, with concentrations ranging from a low of 1.41 µg m⁻³ in the spring to a high of 1.69 µg m⁻³ in the summer (Figure 2.6; Table 2.3). However, seasonal variations were significant at Sydney with concentrations ranging from a low of 0.97 µg m⁻³ in the fall to a high of 2.06 µg m⁻³ in the spring (Figure 2.6; Table 2.3). Spring (March-May) concentrations at Sydney were significantly higher than at Gandy Bridge (p=0.01) (Table 2.4). Fall (September-November) concentrations at Sydney were significantly lower than at Gandy Bridge (p=0.009) (Table 2.4). Winter (December-February) and summer (June-August) concentrations were not significantly different between the two sites. Winter and fall concentrations at Sydney are approximately 30% and 50% lower than spring and summer concentrations. This trend was also discovered by Walker et al. (2004), who found that at a site influenced in part by agricultural emissions of ammonia, concentrations ranged from a low in winter of 0.49 µg m⁻³, to a high in spring of 3.93 µg m⁻³. It is unusual that summer concentrations at Sydney are not significantly different from spring concentrations, considering that research in other locations suggest that peak concentrations occur in the summer season (Burkhardt et al., 1998; Fowler et al., 1998; Robarge et al., 2002). It is possible that frequent summer rainstorms effectively scavenge ammonia from the airshed, thereby lowering average summer concentrations. This relationship suggests that ambient concentrations at Sydney may be affected primarily by agricultural sources because ammonia volatilization is dependent on meteorological
parameters such as ambient temperature. The seasonal cycle is in agreement with the temperature dependence between aqueous and gas-phase ammonia as predicted by Henry’s Law, which results in increasing ammonia emissions from soils and animal waste with increasing temperature (Asman et al., 1998). On the other hand, seasonally consistent ammonia concentrations at Gandy Bridge suggest that this site is affected by a continual source of ammonia and therefore, is likely not influenced by agricultural sources alone. This hypothesis is compatible with literature findings, which suggest that unlike rural concentrations, urban concentrations do not vary seasonally (Fowler et al., 1998; Larsen et al., 2001; Perrino et al., 2002). Walker at al., (2004) found that at a site in North Carolina that was not influenced by agricultural emissions, concentrations did vary slightly by season but at a lower range in concentration from 0.33 µg m⁻³ in the winter to a high of 0.72 µg m⁻³ in the summer.

Likewise, ammonium concentrations at Gandy Bridge did not vary seasonally, with concentrations ranging from 0.82 µg m⁻³ in the fall to 0.96 µg m⁻³ in the spring (Figure 2.7; Table 2.3). Seasonal concentrations at Sydney were consistent except for the fall season when average concentrations were approximately 40% lower than winter and spring, and 25% lower than the summer season. The only statistically significant difference between seasons at Gandy Bridge and Sydney occurred in the fall (p=0.02) (Table 2.4). These results are consistent with those of Walker et al. (2004), who discovered no seasonal variation in ammonium at three research sites in North Carolina. This pattern suggests that ammonium is not affected by meteorological parameters
and is likely a combination of local and long-range transport into the region (Walker et al., 2004).

In Figure 2.8 is shown the fraction of ammonia in the gas phase, which also follows a seasonal trend at both sites. A higher fraction of ammonia is in the gas phase at the Sydney site than at Gandy Bridge, indicating that Sydney is more strongly influenced by local ammonia emissions, especially during the spring and summer seasons when ambient temperatures are elevated. At Gandy Bridge the fraction of ammonia in the gas phase exceeds 0.5 during all seasons, indicating that ammonia is also primarily in the gas phase at this site. The seasonal variability at Gandy Bridge is not as pronounced as at the Sydney site, indicating that this site likely favors aerosol formation due to elevated ambient concentrations of sulfur dioxide. This result supports the hypothesis that Sydney is influenced more by agricultural sources of ammonia whereas Gandy Bridge is influenced more by local industrial and agricultural sources.
Figure 2.6 Seasonal 24-hour Average NH$_3$ Concentrations

![NH$_3$ Concentration Chart](chart1)

- Gandy (n=315)
- Sydney (n=53)

Figure 2.7 Seasonal 24-hour Average NH$_4^+$ Concentrations

![NH$_4^+$ Concentration Chart](chart2)

- Gandy (n=315)
- Sydney (n=53)
Figure 2.8 Seasonal Ratio of NH$_3$ to NH$_3$+NH$_4^+$

- **Gandy Bridge**
- **Sydney**

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### Table 2.3 Seasonal Summary Statistics of 24-hour Average NH$_3$ and NH$_4^+$ Concentrations (µg m$^{-3}$)

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<td>0.38</td>
<td>14</td>
</tr>
</tbody>
</table>

### Table 2.4 Statistically Significant Seasonal Differences Between Gandy Bridge and Sydney Sites

<table>
<thead>
<tr>
<th></th>
<th>Winter</th>
<th>Spring</th>
<th>Summer</th>
<th>Fall</th>
</tr>
</thead>
<tbody>
<tr>
<td>lnNH$_3$</td>
<td>n/a</td>
<td>p=0.01</td>
<td>n/a</td>
<td>p=0.009</td>
</tr>
<tr>
<td>lnNH$_4^+$</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>p=0.02</td>
</tr>
</tbody>
</table>
2.7.3 Diurnal Characteristics

The integrated 12-hour average ammonia concentrations measured at Gandy Bridge and Sydney during May 2002 were used to determine diurnal patterns in ambient ammonia and ammonium concentrations. The average daily and nightly ammonia concentrations at the Gandy Bridge site were $1.59 \pm 1.26 \mu g \text{ m}^{-3}$ and $2.62 \pm 2.55 \mu g \text{ m}^{-3}$, respectively. The average daily and nightly ammonia concentrations at the Sydney site were $2.23 \pm 0.84 \mu g \text{ m}^{-3}$ and $1.17 \pm 0.52 \mu g \text{ m}^{-3}$, respectively (Figure 2.9; Table 2.5). The elevated concentrations during the daytime at Sydney (90% greater than nighttime concentrations) are consistent with diurnal trends discovered in rural locations (Burkhardt et al., 1998; Robarge et al., 2002), although Walker et al. (2004) discovered a conflicting trend with higher concentrations occurring during the nighttime hours at a site influenced by agricultural emissions of ammonia. On the other hand, ammonia concentrations in rural areas are positively correlated with ambient temperature as a result of increased ammonia volatilization from agricultural activities. The elevated nighttime concentrations at Gandy Bridge (65% greater than daytime concentrations) are likely caused by the diurnal shift in sea breeze patterns with winds mainly from the east during the evening hours. Easterly winds may transport ammonia from the source-rich regions of the interior Florida peninsula, whereas, westerly winds from the Gulf of Mexico contain minimal concentrations of ammonia. Walker et al. (2004) hypothesized that research sites located downwind of ammonia sources experienced elevated ambient concentrations due to transport of ammonia into the region. Daytime ammonia
concentrations at Gandy Bridge were significantly lower than at Sydney (p=0.001) and nighttime ammonia concentrations at Gandy Bridge were significantly higher than at Sydney (p=0.06) (Table 2.6).

The average daily and nightly ammonium concentrations at the Gandy Bridge site were 0.64 ± 0.50 µg m⁻³ and 0.56 ± 0.55 µg m⁻³, respectively. The average daily and nightly ammonium concentrations at the Sydney site were 0.56 ± 0.52 µg m⁻³ and 0.82 ± 0.76 µg m⁻³, respectively (Figure 2.10; Table 2.5). Diurnal ammonium concentrations did not vary considerably at Gandy Bridge, however, there was a considerable difference in the average diurnal concentrations at Sydney with 46% higher concentrations in the evening than during the daytime hours. There were no significant differences between ammonium concentrations at Gandy Bridge and Sydney during both the daytime and nighttime hours (p>0.05) (Table 2.6).

In Figure 2.11 is shown the fraction of ammonia in the gas phase, which also follows a diurnal trend at both sites. A higher fraction of ammonia is in the gas phase during the daytime at the Sydney site and a slightly higher fraction of ammonia is in the gas phase during the nighttime at Gandy Bridge. The diurnal variation in ammonia and ammonium concentrations at Gandy Bridge and Sydney cannot be explained by diurnal differences in sulfur dioxide concentrations, as there was no diurnal variation in SO₂ at Gandy Bridge and elevated concentrations during the daytime hours at Sydney. Therefore, it is likely that ammonia concentrations at Sydney are influenced more by ambient temperature whereas at Gandy Bridge they are not.
Figure 2.9 Diurnal 12-hour Average NH$_3$ Concentrations

Figure 2.10 Diurnal 12-hour Average NH$_4^+$ Concentrations
Table 2.5 Diurnal Summary Statistics of 12-hour Average NH₃ and NH₄⁺ Concentrations (µg m⁻³)

<table>
<thead>
<tr>
<th>Site</th>
<th>NH₃</th>
<th>NH₄⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gandy Bridge</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diurnal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>D</td>
<td>1.59</td>
</tr>
<tr>
<td>Median</td>
<td></td>
<td>1.30</td>
</tr>
<tr>
<td>SD</td>
<td></td>
<td>1.26</td>
</tr>
<tr>
<td>n</td>
<td></td>
<td>32</td>
</tr>
<tr>
<td>Night</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>N</td>
<td>2.62</td>
</tr>
<tr>
<td>Median</td>
<td></td>
<td>1.32</td>
</tr>
<tr>
<td>SD</td>
<td></td>
<td>2.55</td>
</tr>
<tr>
<td>n</td>
<td></td>
<td>32</td>
</tr>
<tr>
<td>Sydney</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diurnal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>D</td>
<td>2.23</td>
</tr>
<tr>
<td>Median</td>
<td></td>
<td>1.96</td>
</tr>
<tr>
<td>SD</td>
<td></td>
<td>0.84</td>
</tr>
<tr>
<td>n</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>Night</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>N</td>
<td>1.17</td>
</tr>
<tr>
<td>Median</td>
<td></td>
<td>1.20</td>
</tr>
<tr>
<td>SD</td>
<td></td>
<td>0.52</td>
</tr>
<tr>
<td>n</td>
<td></td>
<td>25</td>
</tr>
</tbody>
</table>

Table 2.6 Statistically Significant Diurnal Differences Between Gandy Bridge and Sydney Sites

<table>
<thead>
<tr>
<th>Day</th>
<th>lnNH₃</th>
<th>lnNH₄⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>p=0.001</td>
<td>n/a</td>
</tr>
<tr>
<td>Night</td>
<td>p=0.06</td>
<td>n/a</td>
</tr>
</tbody>
</table>
2.7.4 Modeling NH$_3$ Concentrations

2.7.4.1 Multiple Linear Regression Analysis

Multiple linear regression analysis is a technique that is used to explore the nature of the relationship between a dependent variable ($y$) and several independent variables ($x_1, x_2, ..., x_q$). The result of the model takes the form:

$$ y = \alpha + \beta_1 x_1 + \beta_2 x_2 + \ldots + \beta_q x_q + \varepsilon $$

(Equation 2.1)

where $\alpha$ is the population intercept, $\beta_1, \beta_2, \ldots, \beta_q$ are the population slopes, and $\varepsilon$ is the random error associated with $y$. The coefficient of determination is represented by $R^2$ or the adjusted $R^2$ and is interpreted as the proportion of the variability among the observed values of $y$ that is explained by the linear regression of $y$ on $x_1, x_2, ..., x_q$ (Pagano and Gauvreau, 1993). To evaluate the 12-hour data sets from Gandy Bridge and Sydney during May 2002, the forward selection process was used by introducing variables into the model one at a time (Kleinbaum et al., 1998). Concentration data were log-transformed to improve fit. The meteorological variables: air temperature, relative humidity, wind speed, and wind direction were examined for their effects on ammonia concentrations at the Gandy Bridge and Sydney sites. The results of the SYSTAT modeling can be found in Appendix A.

The loess-smoothed scatterplots (weighting=0.1) in Figure 2.12 represent graphically the relationships between log-transformed ammonia concentrations...
and meteorological parameters used to construct the model at Gandy Bridge. It is apparent that there was no clear relationship between ammonia concentration and temperature, relative humidity, or wind speed. However, there did seem to be a relationship between concentration and wind direction, with concentrations increasing after 50 degrees and decreasing substantially after 180 degrees. This trend is logical considering that Gandy Bridge is located in an urban setting away from agricultural sources and most of the industrial sources that are influential in the area are to the east and southeast of the site. The relationship between log-transformed ammonia concentration and wind direction suggests that a sine or cosine function was suitable for the following model (Robarge et al., 2002):

$$\ln(NH_3) = \beta_0 + \beta_1 \sin \left( \frac{2\pi WD}{360} \right) + \varepsilon$$

(Equation 2.2)

Model results indicated that the population parameters $\beta_0$ and $\beta_1$ were significantly different from zero and wind direction explained 18.7% of the variability in the observed values of ammonia concentration. Although adding the variable cosine $\left( \frac{2\pi WD}{360} \right)$ increases the adjusted $R^2$ to 0.21, a t-test on the population parameter resulted in no statistically significant difference from zero, therefore this parameter was removed. Likewise, adding temperature, relative humidity, and wind speed to the model separately did not result in a statistically significant difference from zero for their population parameters, therefore, they were not included in the model. However, because several of the parameters
were correlated, interaction terms were added to the model and tested for significance. The addition of the interaction between temperature and humidity (TEMP*HUM) did result in a statistically significant difference from zero and an increase in the adjusted $R^2$ to 0.269. The final model for Gandy Bridge takes the form:

\[
\ln(NH_3) = -1.37 + 0.64 \sin\left(\frac{2\pi WD}{360}\right) + 0.001(TEMP * HUM) + \varepsilon \quad \text{(Equation 2.3)}
\]

where $NH_3$ is in units of $\mu$g m$^{-3}$, wind direction (WD) is in degrees, temperature (TEMP) is in degrees Celsius, and relative humidity (HUM) is in percentage. Wind direction alone explained 18.7% of the variability in the observed values of ammonia concentration. Adding the interaction between temperature and relative humidity explained an additional 8.2% of the variability. The complete model explained 26.9% of the variability in the observed values of ammonia concentration at the Gandy Bridge site (Figure 2.14). See Table 2.7 for multiple regression modeling results.

The same analytical procedure was performed on data measured at the Sydney site. The loess-smoothed scatterplots (weighting=0.1) in Figure 2.13 are a graphical representation of the relationships between log-transformed ammonia concentrations and meteorological parameters used to construct the model at Sydney. There seemed to be a relationship between ammonia concentration and temperature, relative humidity, and wind speed at Sydney. However, there
was no apparent relationship between concentration and wind direction. The relationship between log-transformed ammonia concentration and temperature suggests that a linear function is suitable for the following model:

\[
\ln(NH_3) = \beta_0 + \beta_1(TEMP) + \varepsilon \tag{Equation 2.4}
\]

Model results indicated that the population parameters \(\beta_0\) and \(\beta_1\) were significantly different from zero and temperature explained 28.8\% of the variability in the observed values of ammonia concentration. Although adding the variable wind speed (WS) increases the adjusted \(R^2\) to 0.299, a t-test on the population parameter results in no statistically significant difference from zero, therefore this parameter was removed from consideration. Likewise, adding a sine or cosine function for relative humidity and a linear function for wind direction to the model separately did not result in a statistically significant difference from zero for their population parameters, therefore, they were not included in the model. Interaction terms were also tested for significance. There was no significance found for interactions between temperature and relative humidity or wind speed and wind direction. The final model for Sydney takes the form:

\[
\ln(NH_3) = -1.24 + 0.06(TEMP) + \varepsilon \tag{Equation 2.5}
\]
where NH$_3$ is in units of $\mu$g m$^{-3}$ and temperature (TEMP) is in degrees Celsius. Temperature alone explained 28.8% of the variability in the observed values of ammonia concentration (Figure 2.15). See Table 2.8 for multiple regression modeling results. Figures 2.16 and 2.17 clearly illustrate the influence of wind direction and temperature on ammonia concentrations at the Gandy Bridge and Sydney sites, respectively.
Figure 2.12 Gandy Bridge 12-hour Average Log-transformed Ammonia Concentrations (n=62)
Figure 2.13 Sydney 12-hour Average Log-transformed Ammonia Concentrations (n=49)
### Table 2.7 Results of Multiple Regression Analysis at the Gandy Bridge Site

<table>
<thead>
<tr>
<th>Variable</th>
<th>Coefficient</th>
<th>t-value</th>
<th>P &gt; t</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>-1.37</td>
<td>-2.09</td>
<td>0.040</td>
<td>0.65</td>
</tr>
<tr>
<td>Sin(2\pi WD/360)</td>
<td>0.64</td>
<td>3.93</td>
<td>0.000</td>
<td>0.16</td>
</tr>
<tr>
<td>TEMP*HUM</td>
<td>0.001</td>
<td>2.34</td>
<td>0.023</td>
<td>0.00</td>
</tr>
</tbody>
</table>

### Table 2.8 Results of Multiple Regression Analysis at the Sydney Site

<table>
<thead>
<tr>
<th>Variable</th>
<th>Coefficient</th>
<th>t-value</th>
<th>P &gt; t</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>-1.24</td>
<td>-2.64</td>
<td>0.011</td>
<td>0.47</td>
</tr>
<tr>
<td>TEMP</td>
<td>0.06</td>
<td>3.26</td>
<td>0.002</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Figure 2.14 Parameters that Explain Ammonia Variability at the Gandy Bridge Site

GANDY BRIDGE

- Wind Direction: 19%
- TEMP*HUM: 8%
- Unknown: 73%

Figure 2.15 Parameters that Explain Ammonia Variability at the Sydney Site

SYDNEY

- Temperature: 29%
- Unknown: 71%
Figure 2.16 3-D Mesh Plot of Relationship Between Wind Direction, Temperature*Humidity, and Ammonia Concentration at Gandy Bridge (May 2002)

Figure 2.17 3-D Mesh Plot of Relationship Between Temperature and Ammonia Concentration at Sydney (May 2002)
2.7.4.2 Principal Components Analysis (PCA)

Principal components analysis is a statistical technique that linearly transforms a large dataset containing correlated variables \( (p) \) into a smaller set of uncorrelated variables \( (k) \). The smaller set of variables maximizes the variation in the linear composites of the principal components and represents most of the information contained in the larger set of correlated variables (Dunteman, 1989). The first principal component \( (y_1) \) of the dataset minimizes the sum of the squared distances in the variable space representing the first principal component \( y_1=a_{11}x_1+a_{12}x_2+\ldots+a_{1p}x_p \). The variance of \( y_1 \) is maximized and the sum of squared weights is equal to one \( (\sum (a_{1i})^2=1 \text{ from } i=1 \text{ to } p) \). The second principal component \( (y_2) \) is a line of closest fit to the residuals from the first principal component \( y_2=a_{21}x_1+a_{22}x_2+\ldots+a_{2p}x_p \) (Dunteman, 1989). It involves finding a second weight vector with a maximized variance that is also equal to one \( (\sum (a_{2i})^2=1 \text{ from } i=1 \text{ to } p) \) and uncorrelated with the first principal component. The first two principal components together have the highest possible sum of squared multiple correlations with the \( p \) variables (Dunteman, 1989). PCA was conducted for the May 2002, 12-hour datasets at Gandy Bridge and Sydney to validate the results of the multiple regression analysis. Complete results of the PCA can be found in Appendix B.

Results of the PCA for Gandy Bridge indicated that the log-transformed ammonia concentrations were correlated solely with the sine function of wind direction \( (0.432) \). The first component likely reflected the wind speed and wind direction parameters and accounted for approximately 40.8\% of the variation in
the total dataset. This is consistent with the results of the regression analysis for Gandy Bridge, which indicated that wind direction explained the majority (18.7\%) of the variability in the ammonia concentrations. The Sydney PCA resulted in a correlation between log-transformed ammonia concentrations and temperature (0.537). Again, these results are consistent with the outcome of the regression analysis for Sydney, which resulted in temperature explaining 28.8\% of the variability in the observed values of ammonia concentration.
2.7.5 $\text{SO}_2$ and $\text{HNO}_3$ Correlations

A study was completed to determine if ammonia concentrations at the Gandy Bridge and Sydney sites were correlated with sulfur dioxide and nitric acid, the precursors to ammonium aerosols. In Tampa, the predominant ammonium aerosol is ammonium bisulfate.

In Figures 2.18 and 2.19 are shown the 3-dimensional relationships between the species of interest and wind direction at the Gandy Bridge site. For the relationship between ammonia, sulfur dioxide, and wind direction, a trend is apparent (Figure 2.18). Elevated concentrations exist at wind directions between approximately 50 and 180 degrees, with a noticeable peak in both sulfur dioxide and ammonia between approximately 150 and 180 degrees. Concentrations of both species decrease significantly after approximately 200 degrees, a trend which is explained by the relatively “clean” maritime air masses from the westerly direction over the Gulf of Mexico. The peak at 150 to 180 degrees from the Gandy site is likely sulfur emissions from both the Tampa Electric Company’s (TECO) and the Florida Power & Light Company’s (FPL) coal burning power plants, which are both located in that direction. There is also a clear relationship between ammonia, nitric acid, and wind direction, as shown in Figure 2.19. There are both strong positive and negative correlations between the species at a wind direction of approximately 180 degrees. The contrary correlations are likely caused by the diurnal nature of nitric acid formation, with production occurring in the daytime hours under the influence of the hydroxyl radical and depletion during the evening (Seinfeld and Pandis, 1998). However, it is evident
that a strong source of ammonia and nitric acid is located to the southeast of the Gandy Bridge site. This may be a combination of emissions from two sources, which include ammonia emissions from an abandoned phosphate manufacturing plant and nitrogen oxide emissions (precursors to nitric acid) from the FPL power plant, and are both located between 150 and 180 degrees from the Gandy Bridge site. Again, concentrations decrease significantly after approximately 200 degrees.

In Figures 2.20 and 2.21 are shown the 3-dimensional relationships between the species of interest and wind direction at the Sydney site. For the relationship between ammonia and sulfur dioxide, there does seem to be an apparent correlation with wind direction (Figure 2.20). One peak exists at between 0 and 100 degrees and a smaller peak located between 200 and 250 degrees suggests an influence from the aforementioned power plants. There is a clear relationship between ammonia, nitric acid, and wind direction, as shown in Figure 2.21. A strong correlation exists for a wind direction of between approximately 50 and 100 degrees, and a moderate correlation between approximately 200 and 250 degrees, which is likely the same source that is affecting the Gandy Bridge site.

Based on the results of this study, there is a strong relationship between species concentrations and wind direction at the Gandy Bridge site, with positive correlations apparent from the east and southeast directions. There were no correlations and very low concentrations when wind directions were westerly from the Gulf of Mexico, reinforcing the results of the regression analysis. At the
Sydney site, there seems to be strong correlations in both species at two trajectories, northeast and southwest of the site, demonstrating the influence of distinct sources from these two directions.
Figure 2.18  3-D Mesh Plot of Correlations Between Ammonia, Sulfur Dioxide, and Wind Direction at Gandy Bridge (May 2002)

Figure 2.19  3-D Mesh Plot of Correlations Between Ammonia, Nitric Acid, and Wind Direction at Gandy Bridge (May 2002)
Figure 2.20 3-D Mesh Plot of Correlations Between Ammonia, Sulfur Dioxide, and Wind Direction at Sydney (May 2002)

Figure 2.21 3-D Mesh Plot of Correlations Between Ammonia, Nitric Acid, and Wind Direction at Sydney (May 2002)
2.8 Summary

Seasonally consistent ammonia and ammonium concentrations at the Gandy Bridge site refute Hypothesis 1, because the Gandy Bridge site is located in an urban location and is likely influenced more by a combination of industrial and agricultural sources of ammonia than temperature dependent agricultural sources alone. At Sydney, a site located in a rural suburb of Tampa, the highest average ammonia concentrations occur in the spring and lowest in the fall, also refuting Hypothesis 1. An explanation for this trend may originate with the unique weather patterns in central Florida during the summer season. Severe thunderstorms occur regularly and effectively scavenge ammonia from the atmosphere, thereby reducing average summer concentrations of ammonia. An explanation for the low ammonia concentrations in the fall versus the winter season may be the large influx of winter residents to the state and the resulting increase in vehicular emissions. This trend may cause an increase in the background concentrations of ammonia in the winter season. Further research is necessary to substantiate these hypotheses.

Elevated nighttime ammonia concentrations at the Gandy Bridge site and elevated daytime concentrations at the Sydney site both support and refute Hypothesis 2. The contrary results are a product of site location and source influence. Statistical modeling of concentration data from the two sites indicated that Gandy Bridge and Sydney are influenced significantly by wind direction and temperature, respectively. Due to the effects of meteorological patterns, winds
are typically from the east in the evening hours, except during the passage of cold fronts. These easterly winds transport ammonia gas from the source-rich regions of Hillsborough and Polk counties to the coastal regions of Hillsborough and Pinellas counties, where the Gandy Bridge site is located. Ammonia concentrations at Sydney are influenced by ambient temperature, so elevated concentrations during the daytime hours are a logical result.

Average annual ammonia and ammonium concentrations at the Gandy Bridge and Sydney monitoring sites are similar and comparable with concentrations found in other ecologically sensitive ecosystems, as previously discussed. This does not support Hypothesis 3. The comparable concentrations at Gandy Bridge and Sydney are not consistent with the results of recent research studies, which show that urban locations had significantly higher average ammonia concentrations than rural, or background sites (Larsen et al., 2001; Perrino et al., 2002). This could be a result of an insignificant mobile source impact at the Gandy Bridge site. Large urban areas are usually impacted more by mobile emissions from a variety of constant sources including cars, buses, and trucks.

Multiple linear regression and principal component analysis results support Hypothesis 4. Multiple regression analysis conducted on the Gandy Bridge data indicated that wind direction was the most influential parameter affecting ammonia concentrations, followed by temperature and relative humidity. Wind direction alone explained 18.7% of the variation in ammonia concentration and supports the trends discovered in seasonal and diurnal concentrations at the
site, with elevated nighttime and consistent seasonal concentrations. Principal components analysis conducted on the data resulted in a correlation between ammonia concentration and wind direction and confirms the multiple linear regression findings. The Sydney regression analysis suggests that ambient temperature is the most influential parameter affecting ammonia concentration. Temperature explained 28.8% of the variability in the ammonia concentrations and also supports the trends discovered in the seasonal and diurnal data, with elevated concentrations occurring during the daytime hours and in the spring and summer seasons. Principal components analysis conducted on the data resulted in a correlation between ammonia concentration and temperature and also confirms the linear regression findings.

Correlations between ammonia and its aerosol precursors showed the influence of wind direction at the Gandy Bridge site, with positive correlations occurring when winds were from the east and southeast directions. At the Sydney site, correlations were apparent with winds from the northeast and southwest directions.

The research findings for the Gandy Bridge site are encouraging from a source-control standpoint. Because the site is located adjacent to Tampa Bay, and the findings of this research indicate that Gandy Bridge is influenced by local industrial and agricultural sources located to the east and southeast, it is likely that future ammonia nitrogen reduction strategies will reduce the ambient atmospheric concentrations and ammonia burden to the Tampa Bay estuary.
CHAPTER 3

WET DEPOSITION OF AMMONIUM AT A COASTAL RESEARCH SITE

3.1 Introduction

Inorganic nitrogen in wet deposition is a significant source of nutrients for phytoplankton and has a direct impact on the health of estuaries and coastal water bodies. Poor et al. (2001) estimated an ammonium direct wet deposition rate of 1.7 kg-N ha\(^{-1}\) yr\(^{-1}\) to Tampa Bay. This is almost 24% of the total (wet plus dry) nitrogen deposition rate of 7.3 kg-N ha\(^{-1}\) yr\(^{-1}\) and approximately 40% of the total (wet plus dry) ammonia and ammonium deposition rate of 4.3 kg-N ha\(^{-1}\) yr\(^{-1}\).

An elevated ammonium deposition rate in the summer season may cause a bi-directional ammonia flux in the estuary. During one summer, ammonium concentrations in Tampa Bay were so elevated that a flux from the bay to the atmosphere was calculated. Larsen et al. (2001) discovered that in the Chesapeake Bay estuary, ammonia flux varied seasonally with a net deposition into the water during the winter and a net volatilization into the atmosphere during the summer. In Tampa, on average almost 60% of the yearly rainfall occurs during the months of June, July, August, and September. This suggests that under normal conditions, the majority of ammonium wet deposition to Tampa Bay occurs during these months, coincident with increased algae activity due to elevated bay water temperatures and optimal sunlight conditions. Wet deposition
delivers a considerable quantity of ammonium to the Tampa Bay estuary and has the potential for stimulating algal growth in the ecosystem.

The wet deposition process is very complex and involves reactions that occur both in-cloud and below-cloud between water droplets, gases, and aerosols (Seinfeld and Pandis, 1998). During wet deposition of ammonium, three processes are responsible for wet removal of the compound: interception, scavenging and transport to the surface. Interception occurs when gases and aerosols are brought into contact with condensed water. The species are then scavenged by cloudwater and raindrops either through dissolution of ammonia or absorption of ammonium, and delivered to the Earth’s surface (Oberholzer et al., 1993; Seinfeld and Pandis, 1998). Prior to delivery, raindrops or cloudwater may evaporate to produce new aerosols.

Many studies have been conducted to determine the ratio of aerosol to gas in rainwater, as well as the ratio of in-cloud to below-cloud contributions. Goncalves et al. (2003) found that in the pristine Amazon region of Brazil, the in-cloud scavenging process dominates and the aerosol contribution in precipitation is more than ten times larger than gas for sulfate, nitrate, and ammonium. Wet deposition studies in the Austrian Alps found that in precipitation, particulate ammonium accounted for 49% - 79% of the ammonium concentration, while gaseous ammonia made up the remaining 51% - 21%, respectively (Kasper-Giebl, et al., 1999). Nadim et al., (2002) conducted similar research in Connecticut and concluded that cloudwater concentrations of ammonium contributed between 50% and 80% of the total reduced nitrogen deposition.
Asman (2000) and Lim (1991) concluded that low pH levels existing in clouds increased ammonia solubility, and the rate of ammonium removal by in-cloud scavenging is greater than below-cloud scavenging. Ammonia gas and ammonium particulate air concentrations, as well as, cloudwater and precipitation ammonium were measured for two summer seasons at Mt. Mitchell, North Carolina. Results showed that cloudwater concentrations of ammonium were almost fifteen and ten times greater than precipitation concentrations during the first and second summer seasons, respectively (Aneja et al., 1998).

Ammonium wet deposition rates are dependent on the type of precipitation event that occurs. Frontal storms tend to form and occur over large distances (regional or national in scope) and have longer residence times, affording the opportunity for more in-cloud scavenging of gases and aerosols. Over the Florida peninsula, convective storms normally form locally and therefore exhibit a stronger relationship between rain concentration of ammonium and ground level air concentrations of ammonia (Goncalves et al., 2000; Harrison et al., 1991). Below-cloud scavenging of highly soluble gases, including ammonia, contributes much more to the rainfall concentrations of these gases. During the short time it takes for a raindrop to fall from the cloud base to the ground, highly soluble gases are more readily dissolved in the droplet and reach equilibrium faster than do moderately soluble gases (Asman, 1995).

Past research has discovered that ammonium concentrations decrease with increasing precipitation amount and intensity (Lim et al., 1991; Luo, 2001; Nadim et al., 2002; Prado-Fiedler, 1990). This is due to below-cloud scavenging
of aerosols and gases during the early stages of a precipitation event, thus cleansing the atmosphere and resulting in lower rainwater concentrations during the latter portion of the event. Prado-Fielder (1990) discovered a relationship between ammonium concentration and precipitation in the western Baltic that follows an inverse half-power law. Likewise, ammonium concentrations in precipitation in Connecticut were two to four times higher at 0.05-cm of precipitation than for amounts exceeding 4 cm (Nadim et al., 2002).

Intra-storm variability of a precipitation event can be substantial and may have implications for the collection of precipitation. Lim et al. (1991) measured this variability at a coastal site in Ireland, far from anthropogenic sources, except for vehicular emissions from a nearby sparsely used road. All of the major ions sampled during this rain event showed a rapid decrease in concentration with precipitation, except for ammonium and non-sea salt sulfate. This is contrary to other findings and may be explained by storm characterization. The air mass was associated with a frontal storm of marine origin and therefore likely contained low concentrations of ammonia and ammonium both in-cloud and below-cloud (Lim et al., 1991). Luo (2001) found an inverse relationship between ammonium concentration and precipitation amount in a similar study conducted in Japan. Additionally, in Arizona, sequential rainfall concentrations of ammonium during convective storms were negatively correlated with rainfall amount. Samples were taken during the summer season near an agricultural region of the state. Such conditions explain the substantial decrease in concentration per rainfall event (Dawson, 1978).
Studies involving airflow history with back trajectories indicate that ammonium concentrations are dependent on source density and location. Ammonia gained by storms depends on the intensity of the ammonia sources and the how quickly the storm is moving. In the Chesapeake Bay region, isotopic analysis of precipitation samples revealed that the dominant sources of ammonium in precipitation were fertilizers and animal excreta, with the highest fluxes from a source-rich agricultural region (Russell et al., 1998). Walker et al. (2000) discovered that in North Carolina’s Coastal Plains region, an annual ammonium concentration increase of 9.5% has occurred since 1990 at a rural site densely populated with swine and poultry operations. This annual increase is positively correlated with steadily increasing ammonia emissions from the state’s swine population. A source receptor regression model also found increases in precipitation concentrations of ammonium at sites located as far as 80 kilometers from the research site (Walker et al., 2000). Smith (2003) discovered that in the Tampa area, the lowest ammonium nitrogen fluxes were observed with air masses from the west and south directions, over the Gulf of Mexico. The highest ammonium nitrogen flux was seen with trajectories from the east, where agricultural and industrial ammonia sources are abundant. Therefore, a goal of this study is to determine the rate at which ammonium in precipitation is delivered to the Tampa Bay estuary when convective storms form over the Florida peninsula and are transported from east to west toward the Gulf of Mexico.
3.2 Objectives and Hypotheses

The objectives of this research endeavor were to determine the intra-storm variability of ammonium deposition to the Tampa Bay estuary during convective thunderstorms, to accurately model this variation, and to determine if the transport of ammonium to the estuary via wet deposition contributes to ammonia evasion from Tampa Bay to the surrounding airshed. The research will enable the formulation of a scavenging rate for ammonium when storm trajectories are from the east. The following research questions and hypotheses will be addressed in this chapter:

- What is the intra-storm variability of ammonium in wet deposition to the Tampa Bay estuary from easterly convective thunderstorms?
  - Hypothesis 1: Per event, ammonium concentrations will decrease as precipitation depth increases.

- Can a model be used to determine baseline values of the ammonia scavenging process and represent aqueous phase accumulation of ammonium during summer rain events?
  - Hypothesis 2: Aqueous phase ammonium accumulation can accurately be represented with a model based on the Eulerian framework.

- Does wet deposition of ammonium cause a bi-directional ammonia flux at the air/water interface of Tampa Bay?
  - Hypothesis 3: Wet deposition of ammonium to Tampa Bay can cause a bi-directional ammonia flux in the summer
season when storms are numerous and bay water conditions are optimal.

3.3 Study Location and Duration

At the Gandy Bridge monitoring site, sequential sampling of ammonium in precipitation was conducted and air concentrations of ammonia were measured. Ammonium sampling occurred for five precipitation events that took place during the following dates: July 17, July 18, August 16, August 20, and August 21, 2003 (Table 3.1). Simultaneous 24-hour integrated ammonia gas measurements were made at two heights, 1-m and 6-m, above the water surface. Results from the coincident measurements were used for bi-directional ammonia flux analysis.

3.4 Sample Collection and Analysis

Sequential sampling of ammonium was conducted with a University of Michigan Automated Sequential Precipitation Sampler (Figure 3.1). The sampler is comprised of a rain sensor, plastic funnel, and sampler rack containing eight 1000-ml Nalgene bottles (Figure 3.2). At the start of a rain event, the sensor triggers the opening of the sampler to begin receiving precipitation. Rainwater is collected through a plastic funnel connected to the sampling rack with a 45-cm long rubber hose. The rack is programmed to collect a user-defined volume of precipitation per bottle and event (Table 3.1). Samples were preserved as collected to a pH<2 with concentrated sulfuric acid as specified in Part 4500-NH₃.
of “Standard Methods for the Examination of Water and Wastewater” (Clesceri et al., 1998).

Ambient air concentrations of gaseous ammonia were measured simultaneously at approximately 1-m and 6-m above Tampa Bay with a dual pump URG, Inc., annular denuder system (ADS) as described in Chapter 2 (Figure 1.8). The measurements were made on a seawall, located adjacent to Tampa Bay and the annular denuders were housed in specially constructed PVC containers. The annular denuder located 1-m above the MSL was secured with a rope and attached to a wooden stand at the seawall. The annular denuder located 6-m above the MSL was attached to a 6-m telescoping flagpole that was raised and lowered as needed. Each pump operated at an airflow of 20 L min\(^{-1}\) for approximately 24-hours each sampling period, which was chosen to insure enough mass was collected on each denuder to discern a gradient between the two measurement heights. Each ADS consisted of a 2.5-µm particle aerodynamic diameter cut-point Teflon coated cyclone inlet and two 150-mm long gas denuders connected in series and coated with phosphoric acid to absorb ammonia, as described in Chapter 2.

The precipitation and annular denuder samples were prepared, extracted, and analyzed at the University of South Florida (USF), College of Public Health Environmental Laboratory. The precipitation samples and denuder extracts were analyzed for ammonium by ion chromatography and all samples were stored in Dionex 10-ml vials and refrigerated until analysis.
Precipitation sample bottles were prepared in the laboratory by first adding 3 drops of concentrated sulfuric acid to assure a sample pH<2. Denuders were prepared as described in Chapter 2. Upon return to the laboratory, daily precipitation and denuder extracts were decanted into Dionex autosampler vials for IC analysis.

The precipitation intensity ($I$) was calculated for each sample and was based on the volume of sample collected over the stated time period and the area of the collection apparatus. The cloud base height ($z$) was obtained from NOAA’s National Data Center website (http://nndc.noaa.gov) for Tampa International Airport, which is located approximately 8-km north of the research site. Meteorological parameters were also measured at the Gandy Bridge site as described in Chapter 2.
Figure 3.1 University of Michigan Automated Sequential Precipitation Sampler at the Gandy Bridge Site

Figure 3.2 Precipitation Sampling Rack
3.5 Quality Assurance/Quality Control

After each sampling event, the precipitation sample bottles, funnel/hose and denuders were washed thoroughly with >18 MΩ deionized water. The sample bottles and funnel/hose were dried and stored covered in plastic bags and denuders were soaked with >18 MΩ deionized water until further use. Precipitation sample bottles were numerically labeled according to event sequence. Samples were collected as soon as possible following an event and transported to the laboratory, where they were decanted into Dionex vials that were labeled with corresponding identification numbers and the precipitation date. The rack information, which included per bottle, the sample start and stop times, volume, and ambient temperature, was then downloaded to a computer and saved for future analysis.

Assembled denuders were marked with factory installed identification numbers. A field log was maintained that included the identification numbers, sampling dates, on and off times, flow rates, elapsed time, and pass or failure status of leak tests. Leak tests were performed every time an assembled denuder was installed for operation to insure that the ADS did not contain leaks that would decrease airflow through the assembly. ADS flow rates were calibrated bi-weekly, unless a problem was noted with the daily flow check. Airflow was mass-controlled within 2% of the set flow rate (URG, 1996).

A field blank was conducted with each precipitation event sampled. Laboratory and field blanks were conducted each time denuders were processed
to diagnose methodological problems. Both laboratory and field blanks were typically a factor of 10 or more below the sample concentrations. During IC analysis, ammonium check standards were run every ten samples and at the beginning and end of each sequence. Additionally, every ten samples, one of the samples was injected twice as a measure of reproducibility. Standards were within 10% of the set concentrations and reproducibility of the duplicates was within 3%. Water was also injected every 10 samples to check for carryover.

Estimates of uncertainty on approximately 6 years of collocated ADS denuder measurements in the Tampa region showed a 15% relative precision for ammonia (n=315). Walker et al. (2004) report less than 10% relative variability for denuder measurements of ammonia (n=90). Only gradient measurements outside of 10% were utilized for comparison, and for measurements within this range, a zero gradient was assumed. As described in Chapter 2, collocated 24-hour integrated measurements at a flow rate of 20 L min\(^{-1}\) resulted in a denuder absorption efficiency and relative precision of 96% and 16%, respectively. These results indicate that there is an insignificant loss of ammonia from the coating layer of the denuder at flow rates up to 20 L min\(^{-1}\). Bias in the precipitation samples may result from the sensitivity of the rain sensor in which a delay in the opening of the sampler may cause a loss of the first drops of rain (Lim et al., 1991). This bias likely results in an underestimation of precipitation ammonium and ambient air ammonia concentrations.
3.6 Aqueous Phase Accumulation of Below-cloud Ammonia

3.6.1 Model Description

During a precipitation event ammonia gas that is present in the atmosphere will dissolve into raindrops, and ammonium particles are also collected as they collide with the drops. Both processes result in the transport of ammonia and ammonium to the Earth’s surface. The rate of accumulation of ammonium is dependent on the event characteristics, the ambient particulate and gas-phase ammonia concentrations, and the physical and chemical properties of ammonia (Seinfeld and Pandis, 1998).

The following model is based on the work of Kumar (1985) and a complete theoretical description can be found in Seinfeld and Pandis (1998). The model determines the rate at which ammonia gas is scavenged from the atmosphere below a storm cloud. The rate of transfer from ammonia gas to a falling drop at a given elevation (z) and time (t) is written as,

$$W_{NH3}(z, t) = K_c \left( C_{NH3}(z, t) - \frac{C_{NH4}(z, t)}{H} \right)$$  \hspace{2cm} (Equation 3.1)

where $C_{NH3}$ is the gas-phase ammonia concentration, $\frac{C_{NH4}(z, t)}{H}$ or $C_{eq}$ is the concentration of ammonia at the droplet surface in equilibrium with the aqueous-phase concentration and $C_{NH4}$ is the aqueous phase ammonium concentration, $H$ is the Henry’s Law constant for ammonia, and $K_c$ is the mass transfer coefficient for ammonia.
Ammonia was assumed an irreversibly soluble gas \( C_{NH3} \gg C_{eq} \) because of its large effective Henry's Law constant \( H^*_{NH3} \geq 1 \times 10^6 \) at pH levels below 5 (typically found in rainwater at the Gandy Bridge site) and the resulting order of magnitude difference between the ambient ammonia gas concentrations \( C_{NH3} \geq 7 \times 10^{-10} \text{ atm} \) and equilibrium concentrations of ammonia at the droplet \( C_{eq} \leq 9 \times 10^{-11} \text{ atm} \). Therefore, the flux from the aqueous to the gas phase can be neglected and Equation 3.1 becomes,

\[
W_{NH3}(z, t) = K_c(C_{NH3}(z, t))
\]  
(Equation 3.2)

The rate of increase of ammonium in a droplet with diameter \( D_p \), is equal to the rate of transport of species to the drop,

\[
\frac{1}{6} \pi D_p^3 \frac{dC_{NH4}}{dt} = \pi D_p^2 W_t
\]  
(Equation 3.3)

therefore, the rate of increase of ammonium concentration in a droplet is given by,

\[
\frac{dC_{NH4}}{dt} = \frac{6K_c}{D_p} C_{NH3} \cdot
\]  
(Equation 3.4)
From the chain rule, the independent variable can be changed from time to height,

\[
\frac{dC_{NH4}}{dt} = \frac{dC_{NH4}}{dz} \frac{dz}{dt} = U_t \frac{dC_{NH4}}{dz} \tag{Equation 3.5}
\]

where \( z \) is the distance from the cloud to the ground and,

\[
\frac{dC_{NH4}}{dz} = \frac{6K_c}{U_tD_p} C_{NH3} \tag{Equation 3.6}
\]

After integrating through height (\( z \)) Equation 3.6 becomes,

\[
C_{NH4} = C^{o}_{NH4} + \frac{6K_cC_{NH3}}{U_tD_p} z \tag{Equation 3.7}
\]

indicating that the concentration through fall distance varies linearly with height (Seinfeld and Pandis, 1998).

Some assumptions inherent in Equation 3.7 are that ammonia gas concentrations are uniform throughout the mixed layer and the droplet diameter remains constant as the drop falls through the atmosphere. Based on the Marshall-Palmer droplet size distribution, the predominant droplet radius is related to rainfall intensity, \( I \) (mm hr\(^{-1}\)), through the equation (Mason, 1971),

\[
r_p(mm) = 0.3659I^{0.21}, \tag{Equation 3.8}
\]
and terminal velocity ($U_t$) is dependent on droplet radius, as shown by Beard and Pruppacher (1969), who determined the terminal velocity of small water drops falling in water-saturated air based on a relationship with the Stokes drag coefficient.

From Kumar (1985), the gas-phase ammonia concentration decreases exponentially with time based on the scavenging coefficient ($\beta$), a parameter that describes the rate at which gas-phase ammonia is scavenged by precipitation. The equation is given by,

$$C_{NH_3} = C_{NH_3}^0 \exp(-\beta t) \quad \text{(Equation 3.9)}$$

and can be substituted into Equation 3.7 for aqueous-phase concentration,

$$C_{NH_4} = C_{NH_4}^0 + \frac{6K_{c}z}{U_tD_p}(C_{NH_3}^0 \exp(-\beta t)) \quad \text{(Equation 3.10)}$$

where $\beta$ is dependent on the rainfall intensity ($I$) and gas-phase mass transfer coefficient ($K_c$) and is given by (Kumar, 1985),

$$\beta = 4\pi r_p^2 N_p K_c \quad \text{(Equation 3.11)}$$

where $r_p$ and $N_p$ are the droplet radius and size distribution, respectively.
3.6.2 Model Application

The model was altered for the time-averaged sequential samples collected during this study. The initial ammonium concentration was not considered in the analysis \( C_{\text{NH}_4}^0 = 0 \) due to a lack of information about in-cloud concentrations of ammonium. Since Equation 3.10 gives ammonium concentrations in a droplet and the experimental data are concentrations of ammonium in collected samples, the model was integrated over each sample collection period \( (t_{si} = t - t_{oi}) \) as,

\[
C_{\text{NH}_4 \text{Avgi}} = \frac{3K_c C_{\text{NH}_4}^0 Z}{U_i r_p t \beta} \left[ \exp\left(-\beta t_{oi}\right) - \exp\left(-\beta t\right) \right]
\]  

(Equation 3.12)

where \( C_{\text{NH}_4 \text{Avgi}} \) is the average concentration of ammonium in each sample bottle. Substituting for \( \beta \) the equation becomes,

\[
C_{\text{NH}_4 \text{Avgi}} = \frac{3C_{\text{NH}_4}^0 Z}{4\pi r_p^3 U_i N_p t} \left[ \exp\left(-\beta t_{oi}\right) \left(1 - \exp\left(-\beta t\right)\right) \right]
\]  

(Equation 3.13)

It can be shown that precipitation intensity is dependent on the rainfall size distribution and terminal velocity of the raindrops as \( I = U_i N_p \frac{4\pi r_p^3}{3} \) (Kumar, 1985). Therefore, the final equation becomes,
where $t_{si}$ is the sample time in minutes, $t_{oi}$ and $t_{fi}$ are the initial and final sampling times for each sample bottle.

Data from the five precipitation events were used to assess the model. The initial concentration ($C_{ori}^{0}$) was eliminated by forcing the total mass of ammonia collected experimentally over a rain event to equal the calculated value as follows:

\[
C_{NH4Avgi} = \frac{C_{ori}^{0}t}{l}[\exp(-\beta t_{oi})(1-\exp(-\beta t_{fi}))]
\]  

(Equation 3.14)

where $C_{ori}^{0}$ is the volume of sample bottle $i$ (ml), $V_{acci}$ is the accumulated volume of previous samples (ml), and $\alpha = \frac{\beta}{A_t l}$ with $A_t$ equal to the area of the sampler collecting raindrops (cm$^2$). The model was applied to the five sequential sampling events to determine the unique relationship between the below-cloud scavenging coefficient for ammonia gas and rain intensity. The resulting relationship was obtained by finding the value of $\alpha$ that minimized the sum of the squares of the differences between experimental and modeled ammonium concentrations given in Table 3.4 and obtained from Equation 3.15 for each rainfall event. Average rainfall intensities for each event were used in these
calculations. A power law relationship between $\beta$ and $I$ was then assumed and the five data points were used to determine the relationship,

$$\beta = 0.08I^{0.66}$$  \hspace{1cm} \text{(Equation 3.16)}

with an $R^2$ value of 0.88.

The calculated Tampa Bay storm event data were compared with results from the Asman (1995) model. This model was developed to compute below-cloud scavenging coefficients of soluble gases during convective thunderstorms. The unique characteristics of this model are that scavenging coefficients are calculated as a function of gas diffusivity at 25°C, meteorological parameters, and rainfall rates at ground level as,

$$\beta = aI^b$$  \hspace{1cm} \text{(Equation 3.17)}

where $I$ is the rainfall intensity (mm hr$^{-1}$) and $a$ and $b$ are calculated based on the air temperature, relative humidity, and gas diffusivity during a storm event (Asman, 1995). The Asman model uses the Best distribution to calculate the raindrop size distribution, which is different from the Marshall-Palmer size distribution used in the Kumar model.

The below-cloud scavenging of aerosol ammonium was considered negligible during this study because of the distinctive characteristics of wet scavenging of fine ammonium particles. A theory called the “Greenfield gap”
hypothesizes that scavenging of particles in the 0.1 to 1.0-\(\mu\)m size range is relatively slow, compared to the efficient scavenging of particles smaller than 0.2-\(\mu\)m and larger than 1.0-\(\mu\)m, which are controlled by Brownian diffusion and inertial impaction, respectively (Seinfeld and Pandis, 1998). In Tampa, ammonium is found predominately in the fine particle size mode of 0.5-\(\mu\)m (Campbell et al., 2002). Based on the average rainfall intensity measured during this study, the mean droplet diameter was calculated with Equation 3.8 and found to be 1.6-mm. Using this diameter and Figure 20.11 in Seinfeld and Pandis (1998), the scavenging coefficient for 0.5-\(\mu\)m ammonium particles was estimated to be 1x10^{-4} h^{-1} or 1.6x10^{-6} min^{-1}, which is several orders of magnitude lower than the modeled gas scavenging coefficients of between 0.01 to 0.2 min^{-1} for ammonia gas (Figure 3.13).

3.7 Results and Discussion

3.7.1 Ammonium Characteristics in Precipitation

All of the five precipitation events for which sequential samples were obtained were typical convective summer thunderstorms for the central, west coast of Florida. All formed in the middle of the peninsula under the effects of the land-sea breeze and moved to the west toward the Gulf of Mexico. For each of the five convective thunderstorms, ammonium concentrations decreased rapidly over time (Figures 3.3-3.7), with a few exceptions. During the July 17\textsuperscript{th} and August 20\textsuperscript{th} rain events, an increase in concentration occurred toward the end of the sampling event. Conversely, during the August 21\textsuperscript{st} rain event, a sizeable
decrease in concentration occurred at the beginning of the sampling event followed by an increase, and then the continued trend of decreasing concentration with time. These anomalies are unexplained and may be a result of sampling errors, varying meteorological conditions, or in-cloud and below-cloud scavenging processes (Lim et al., 1991).

A change in concentration may be caused by contamination of the sample bottle, transportation of fresh ammonia into the airshed due to a change in wind speed or wind direction, or a difference in droplet size resulting in increased or decreased scavenging of in-cloud and below-cloud concentrations of ammonium. An increase in concentration in the 6th sample during the July 17th event corresponds with a decrease in precipitation intensity to 0.14 mm min\(^{-1}\), indicating a decrease in droplet size during that sampling period (Table 3.1).

The changes in concentrations during the August 20th and 21st events cannot be explained by varying precipitation intensities (Table 3.1). It is unlikely that changes in meteorological conditions during the sampling events affected the ammonium concentrations because for all events, average winds were consistently from the east/northeast/southeast directions during, one hour prior to, and following the precipitation. If the winds had changed from easterly to maritime westerly, this assumption may have been valid.

For each of the sampling periods, a power regression relationship was derived between the ammonium concentration in rainwater (\(C_{\text{NH}_4}\)) and cumulative precipitation depth (\(D\)) of the form:
\[ C_{\text{NH}_4} = aD^{-b} \]  
(Equation 3.18)

where \( C_{\text{NH}_4} \) is in mg L\(^{-1} \) and \( D \) is in mm (Figures 3.3-3.7). Four of the five relationships show a strong correlation between concentration and precipitation depth, with the coefficient of determination (\( R^2 \)) values ranging from 0.72 to 0.94. These results are consistent with those of Dawson (1978) and Luo (2001), who measured ammonium concentrations in convective showers in Arizona and Japan, respectively, and found similar trends of decreasing concentration with precipitation depth. The large initial decrease in concentration is likely due to below-cloud rainout of ammonia gas from the airshed, with the remaining samples representative of in-cloud ammonia and ammonium scavenging (Dawson, 1978; Lim et al., 1991). On August 21\(^{st}\), an unusual relationship is evident (Table 3.2; Figure 3.7). Aside from the initial concentration, the relationship follows a parabolic trend. There appears to be an initial washout of ammonia gas, but concentrations in the remaining samples are not consistent with other precipitation events and past research in this field of study (Dawson, 1978). Future research is needed to determine if this is an actual trend or an anomaly.

In Figure 3.8, the cumulative ammonium deposition is compared with the cumulative precipitation for the five events. For all of the events, a range of between 35% and 60% of the ammonium is deposited during the initial 20% of precipitation. This is comparable with the findings of Lim et al. (1991), who
discovered that approximately 47% of precipitation ammonium is deposited during the initial 17% of rainfall.
Table 3.1 Precipitation Event Characteristics (Experimental Data)

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<th>Precipitation Intensity (mm min⁻¹)</th>
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</table>
Figure 3.3 Sequential NH₄⁺ Concentrations on July 17, 2003

\[ y = 1.73x^{-0.49} \]

\[ R^2 = 0.72 \]

Figure 3.4 Sequential NH₄⁺ Concentrations on July 18, 2003

\[ y = 0.63x^{-0.57} \]

\[ R^2 = 0.89 \]
Figure 3.5 Sequential NH$_4^+$ Concentrations on August 16, 2003

\[ y = 2.12x^{-0.96} \]
\[ R^2 = 0.94 \]

Figure 3.6 Sequential NH$_4^+$ Concentrations on August 20, 2003

\[ y = 1.25x^{-0.80} \]
\[ R^2 = 0.82 \]
Figure 3.7 Sequential NH$_4^+$ Concentrations on August 21, 2003

\[ y = 1.47x^{-0.97} \]
\[ R^2 = 0.52 \]

Table 3.2 Experimental Sequential NH$_4^+$ Concentrations (mg L$^{-1}$)

<table>
<thead>
<tr>
<th>Sample</th>
<th>July 17</th>
<th>July 18</th>
<th>August 16</th>
<th>August 20</th>
<th>August 21</th>
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<tbody>
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</tr>
<tr>
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<td>0.65</td>
<td>0.14</td>
<td>0.13</td>
<td>0.17</td>
<td>0.17</td>
</tr>
<tr>
<td>5</td>
<td>0.57</td>
<td>0.11</td>
<td>0.13</td>
<td>0.21</td>
<td>0.15</td>
</tr>
<tr>
<td>6</td>
<td>0.98</td>
<td>0.09</td>
<td>0.13</td>
<td>0.07</td>
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<tr>
<td>7</td>
<td>0.65</td>
<td>0.11</td>
<td>0.11</td>
<td>0.07</td>
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<td>0.01</td>
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</tr>
</tbody>
</table>
Figure 3.8 Cumulative Deposition of $\text{NH}_4^+$ as a Function of Rainfall

Cumulative Rainfall (% of total)

Cumulative $\text{NH}_4^+$ Deposition (% of total)

- July 17
- July 18
- August 16
- August 20
- August 21
3.7.2 Comparison with AIRMoN Samples

The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) is a nationwide network of precipitation monitoring sites. The network is a cooperative effort between the State Agricultural Experiment Stations, U.S. Geological Survey, U.S. Department of Agriculture, and numerous other governmental and private entities. The purpose of the network is to collect data on the chemistry of precipitation for monitoring of geographical and temporal long-term trends. The Atmospheric Integrated Research Monitoring Network (AIRMoN) was formed under NADP/NTN for the purpose of studying precipitation chemistry trends with greater temporal resolution. Precipitation samples are collected daily from a network of nine sites, including Gandy Bridge, and analyzed for hydrogen (acidity as pH), sulfate, nitrate, ammonium, chloride, and base cations (such as calcium, magnesium, potassium and sodium). The Gandy Bridge site (FL18) has been operational for AIRMoN since 1996 (NOAA, 2003). Additional program information is available at the NADP/NTN website (http://nadp.sws.uiuc.edu/).

Gandy Bridge AIRMoN samples collected simultaneously with sequential samples were compared to determine if diverse sampling techniques affect concentration results. The differences between the two techniques are as follows:

- AIRMoN samples are collected once every 24-hours and may contain rainfall from several precipitation events that have occurred
during that time period; sequential samples were collected based on a user-defined volume per precipitation event.

- AIRMoN samples were not preserved as collected; sequential samples were preserved with sulfuric acid to prevent chemical and/or biological transformations.
- AIRMoN samples were collected daily and stored chilled for up to one week until shipped to the Illinois State Water Survey located in Champaign, Illinois; sequential samples were collected, chilled, and analyzed at the University of South Florida following a rain event.

The results of the comparison are shown in Table 3.3. On average, the AIRMoN samples are between approximately 50% and 95% of the sequential ammonium concentrations. These differences suggest that chemical and/or biological transformations may be occurring in the AIRMoN samples. The biological transformation of ammonium to nitrate may occur during the time it takes to collect, transport, and analyze the samples. In summary, the AIRMoN sampling protocol produces results that may underestimate wet deposition estimates of ammonium to the Tampa Bay estuary.
<table>
<thead>
<tr>
<th>Event</th>
<th>AIRMoN</th>
<th>Volume Weighted Average Sequential</th>
<th>Ratio AIRMoN/Sequential</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 17, 2003</td>
<td>0.68</td>
<td>0.91</td>
<td>0.75</td>
</tr>
<tr>
<td>July 18, 2003</td>
<td>0.17</td>
<td>0.18</td>
<td>0.94</td>
</tr>
<tr>
<td>August 16, 2003</td>
<td>0.15</td>
<td>0.29</td>
<td>0.52</td>
</tr>
<tr>
<td>August 20, 2003</td>
<td>0.21</td>
<td>0.26</td>
<td>0.80</td>
</tr>
<tr>
<td>August 21, 2003</td>
<td>0.12</td>
<td>0.19</td>
<td>0.63</td>
</tr>
</tbody>
</table>
3.7.3 Aqueous Phase Accumulation Model

A comparison between the measured ammonium concentrations and the modeled values are presented in Table 3.4 and Figures 3.9-3.13. Generally, the model (Equation 3.15) represented well the sequential concentrations of ammonium for each event. When concentrations exceeded 0.5 mg L\(^{-1}\), the model becomes less accurate by both under and over predicting the ammonium concentrations in precipitation. The reduction in efficiency for increased ammonium concentrations may lie in the assumption of uniform gas concentration throughout the mixed layer. This may not hold true when elevated concentrations of ammonia gas are transported into the area from a source-rich region. If an atmospheric gradient exists and elevated ammonia concentrations are located closer to the ground as expected, then scavenging rates will be affected.

In Figure 3.14 is shown the results of the relationship between rain intensity (I) and scavenging coefficient (\(\beta\)) (Equation 3.16) for the five sequential sampling events analyzed in this section. The Asman model compared well with the Tampa Bay model (Table 3.5). This would indicate that the Best drop size distribution, used in the Asman model, accurately represents raindrop size distributions in convective storms in the Tampa Bay estuary. However, the relative percent difference increases for rainfall intensities greater than 2.0 mm min\(^{-1}\), with the Asman model under predicting scavenging coefficients at these high rainfall rates. The Best drop size distribution is only valid up to a rainfall intensity of 2.5 mm min\(^{-1}\), which might explain the increasing disparity (Asman, 113...
1995). Overall, the Tampa Bay scavenging rate model is a useful tool for calculating below-cloud scavenging of ammonia during convective thunderstorms, as is evidenced by the reasonable agreement with the Asman model as shown in Figure 3.14. The ammonia scavenging coefficient algorithm developed during this study will replace the default values used in the ISC Short Term Wet Deposition model and the CALPUFF dispersion model for Tampa Bay.

The altered model, Tampa Bay scavenging coefficients, and experimental rainwater concentrations were used to calculate the initial ambient ammonia concentrations \( (\text{C}_{\text{NH}_3}^0) \) for each rain event (Equation 3.14). These concentrations were compared with 24-hour integrated ammonia concentrations measured with an ADS at the Gandy Bridge site prior to the start of each rain event (Table 3.6; Figure 3.15). Based on rainfall data, the modeled ambient ammonia concentrations are approximately two to five times greater than the measured concentrations. This is likely due to the difference between the 24-hour averaged monitoring period in which the air measurements were collected and the modeled value which represents the air concentration prior to the start of the rainfall event. In addition, there likely existed a considerable in-cloud concentration of ammonium that is contributing to an increased total ammonium concentration in the experimental samples. As previously discussed, the convective storm events all formed over the source-rich regions of the state, which likely contributed to elevated in-cloud concentrations. Whereas, storm cells that form over non-polluted areas contain low in-cloud concentrations of
pollutants, resulting in a better correlation between modeled and measured values (Goncalves et al., 2000).

Based on the results of this study, one should feel reasonably confident in the use of this model to represent below-cloud scavenging of ammonia by convective thunderstorms. The model is not as robust, however, when rainwater concentrations of ammonium exceed 0.5 mg L\(^{-1}\). It is yet to be determined if rainfall concentrations follow the same patterns when produced by frontal storms of marine origin, which typically occur in the fall, winter, and early spring seasons. Additional research is needed to determine if this model can be used for these types of rainfall events.
<table>
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<th>Modeled</th>
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Figure 3.9 Comparison Between Experimental and Modeled Sequential Rainwater Concentrations – July 17, 2003

Figure 3.10 Comparison Between Experimental and Modeled Sequential Rainwater Concentrations – July 18, 2003
Figure 3.11 Comparison Between Experimental and Modeled Sequential Rainwater Concentrations – August 16, 2003

Figure 3.12 Comparison Between Experimental and Modeled Sequential Rainwater Concentrations – August 20, 2003
Figure 3.13 Comparison Between Experimental and Modeled Sequential Rainwater Concentrations – August 21, 2003
Table 3.5 Comparison Between Tampa Bay and Asman Modeled Scavenging Coefficients ($\beta$ (min$^{-1}$))

<table>
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<tr>
<th>Event</th>
<th>Intensity (mm min$^{-1}$)</th>
<th>Tampa Bay Model</th>
<th>Asman Model</th>
<th>Relative % Difference</th>
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<td>1.83</td>
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<td>0.82</td>
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Figure 3.14 Comparison Between Precipitation Intensity (I) and Scavenging Coefficient (β) for the Tampa Bay and Asman Models and their Associated Error Bars at 95% Confidence
Table 3.6 Comparison Between Experimental and Modeled Ambient NH$_3$ Concentrations (µg m$^{-3}$)

<table>
<thead>
<tr>
<th>Event</th>
<th>Experimental</th>
<th>Modeled</th>
<th>Ratio Modeled/Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 17, 2003</td>
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<td>17.1</td>
<td>4.8</td>
</tr>
<tr>
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</tr>
<tr>
<td>August 21, 2003</td>
<td>2.7</td>
<td>5.2</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Figure 3.15 Comparison Between Experimental and Modeled Ambient NH$_3$ Concentrations
3.7.4 Bi-directional Ammonia Flux Analysis

The wet flux of ammonium was calculated for each of the five precipitation events, and compared with the atmospheric ammonia gradient measurements made for each event. A negative atmospheric ammonia gradient was observed when the denuder concentration at 1 m above the MSL was greater than the concentration at 6 m above the MSL. The results of the bi-directional ammonia flux analysis are shown in Figure 3.16. All of the calculated atmospheric gradients were between 10% and 20% measurement errors, except for the August 21st gradient, which was within a 10% measurement error. For four of the five events, a negative ammonia gradient was calculated, indicating that ammonia was emitted from the bay to the airshed. On August 21, 2003, a positive ammonia gradient occurred, indicating ammonia deposition to the bay. Upon further analysis, it was determined that during the 24-hour sampling period from August 21st through August 22, 2003, prevailing winds were from the east direction. As discussed in Chapter 2, easterly winds transport ammonia from the source-rich regions of Hillsborough and Polk counties to the Gandy Bridge site, which probably contributed to the positive ammonia gradient observed during this sampling period.

Wet deposition of ammonium alone may not cause a negative ammonia flux. Known as indirect deposition, considerable quantities of ammonium are transported to the bay through precipitation runoff from land surfaces. Since measurements were made on a seawall at the Gandy Bridge site, surface runoff from these events likely contributed and should be considered along with direct
wet deposition when determining the contribution of wet deposition to bi-directional ammonia flux estimates.
Figure 3.16 Relationship Between Wet NH$_4^+$ Flux and Atmospheric NH$_3$ Gradient

<table>
<thead>
<tr>
<th>Date</th>
<th>Wet Flux (kg-NH4/ha)</th>
<th>Atmospheric Gradient (8m-1m) (ug-NH3/m3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/17/03</td>
<td>2.0</td>
<td>-0.5</td>
</tr>
<tr>
<td>7/18/03</td>
<td>1.0</td>
<td>-0.5</td>
</tr>
<tr>
<td>8/16/03</td>
<td>2.5</td>
<td>-0.5</td>
</tr>
<tr>
<td>8/20/03</td>
<td>1.5</td>
<td>0.0</td>
</tr>
<tr>
<td>8/21/03</td>
<td>1.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
3.8 Summary

The trend of decreasing ammonium concentration with increasing precipitation depth supports Hypothesis 1. The results of this study are similar to past research conducted on this topic that found a substantial decrease in ammonium concentration during the initial stages of a rainfall event with smaller increments of decreasing concentration during the latter portions of the event (Lim et al., 1991; Nadim et al., 2002; Prado-Fiedler, 1990). The significant decrease in ammonium concentration during the initial stages of each event represent the below-cloud scavenging of ammonia gas, since ammonium aerosols were considered negligible due to a low scavenging rate. The events sampled during this study were all convective thunderstorms that formed over the center of the state and moved west toward the Gulf of Mexico. Future research on frontal storms that typically occur during the fall, winter, and spring seasons is necessary to determine if ammonium concentrations also follow a power regression relationship for this category of storms. These results show that during convective storms following an easterly trajectory, the majority of ammonium is delivered to Tampa Bay during the initial stages of the storm. Future controls on ammonia sources located to the east of the estuary will likely reduce the rate at which ammonium is wet deposited to Tampa Bay. This data provides a baseline for determining the beneficial effects of ammonia reduction strategies on the wet deposition process.

An aqueous phase accumulation model was used to represent sequential ammonium concentrations at the Gandy Bridge site. The model results showed
reasonable agreement when compared with actual samples collected during this research study, which supports Hypothesis 2. The model was more precise when ammonium concentrations were less than 0.5 mg L$^{-1}$. At higher concentrations, the scavenging rate of ammonia gas may not be uniform over the cloud-to-ground distance due to a gradient caused by elevated concentrations of ammonia gas at the surface. A relationship between rainfall intensity and scavenging coefficient was developed and will enable the calculation of this important input parameter for future studies that explore the relationship between wet deposition and nitrogen reduction strategies. The ammonia scavenging coefficient algorithm developed during this study will replace the scavenging coefficients used in the ISC Short Term Wet Deposition model the CALPUFF dispersion model for Tampa Bay.

The wet flux of ammonium was compared with atmospheric ammonia gradient measurements for the five events analyzed in this study. The results of the analysis indicate that for four of the five events, a positive correlation exists between the wet flux of ammonium and ammonia emissions from the bay to the airshed, supporting Hypothesis 3. This bi-directional flux estimate suggests that direct and indirect wet deposition of ammonium to Tampa Bay may cause ammonia to be emitted from the bay during the summer season.

Finally, based on a comparison of AIRMoN and sequential samples collected simultaneously and analyzed for ammonium concentrations, it was discovered that AIRMoN samples are between approximately 50% and 95% of the ammonium concentrations in the sequential samples. This disparity may be
the result of the biological transformation of ammonium to nitrate during sample collection and transport. These differences indicate that based on AIRMoN sampling, calculations of the wet flux of ammonium to the Tampa Bay estuary may be consistently underestimated.
CHAPTER 4
THE NOAA BUOY MODEL - EVALUATION AND IMPROVEMENT

4.1 Introduction

4.1.1 Dry Deposition of Atmospheric Gases

The dry deposition of ammonia to Tampa Bay occurs when the species is transported from the atmosphere to the water surface in the absence of precipitation. Dry deposition flux is governed by the following equation (Liss and Slater, 1974):

\[ F = v_d \left( C_{\text{air}} - C_{\text{eq}} \right) \]  \hspace{1cm} (Equation 4.1)

where \( F \) represents the constant vertical dry flux to the reference height in unit surface area per unit time, \( C_{\text{air}} \) is the concentration of ammonia at some reference height above the water surface (µg m\(^{-3}\)), \( C_{\text{eq}} \) is the concentration of ammonia, just above the water surface, that is in equilibrium with the bay water ammonium concentration (µg m\(^{-3}\)), and \( v_d \) is the deposition velocity in (cm s\(^{-1}\)). A negative flux indicates an ammonia flux from the bay to the airshed.

The deposition velocity, or transfer rate, is controlled by the level of turbulence in the atmosphere, especially in the layer nearest to the ground (Seinfeld and Pandis, 1998). The three processes that contribute to the value of...
the deposition velocity include: (1) aerodynamic transport through the atmospheric surface layer to a thin layer of stagnant air just above the surface, by turbulent diffusion; (2) transport across this thin layer, also called the quasi-laminar boundary layer, by molecular diffusion; and (3) uptake at the surface (Seinfeld and Pandis, 1998). The transport of a gas to the water surface is represented as a series of resistances in each of the three transport processes as follows (Figure 4.1):

1. aerodynamic resistance \( r_a \)
2. quasi-laminar layer resistance \( r_b \)
3. surface or canopy resistance \( r_c \)

The deposition velocity is related to the total resistance as,

\[
\frac{1}{v_d} = r_t = r_a + r_b + r_c \quad \text{(Equation 4.2)}
\]

Aerodynamic resistance \( r_a \) is dependent on turbulence intensity in the atmospheric boundary layer, which is governed by atmospheric stability and surface roughness. Parameters that are measured to determine these meteorological characteristics include wind speed, air and water temperature, relative humidity, radiation, and surface roughness length (Seinfeld and Pandis, 1998). It is assumed that turbulent transport of gases is similar to transport mechanisms for heat, moisture, and momentum in the atmosphere (Arya, 1988). Using scaling techniques, measurements made for these parameters can be utilized to calculate the behavior of gases, also known as similarity theory.
Typically over land, aerodynamic resistance follows a strong diurnal cycle with resistance decreasing during the daytime when prevailing winds are more active, and increasing during the evening hours when winds are lighter and the atmosphere becomes more stable (Seinfeld and Pandis, 1998). However, over water bodies, $r_a$ does not vary as dramatically on a diurnal cycle due to the temporal homogeneity of temperature caused by the large heat capacity of water (Arya, 1988). Consequently, as fetch and water body increase in size, the diurnal cycle of $r_a$ decreases. The quasi-laminar resistance ($r_b$) depends on the molecular diffusivity of the gas being considered, with molecular diffusivity represented by the Schmidt number (Seinfeld and Pandis, 1998). It is hypothesized that as wind speed increases, $r_b$ decreases as the depth of the quasi-laminar layer shrinks in response to turbulent shear stresses near the surface. Surface resistance ($r_c$) is also dependent on the characteristics of the gas being analyzed. Because ammonia is a highly soluble gas, surface resistance is negligible compared to aerodynamic and quasi-laminar resistance, and is therefore removed from consideration in most cases (Buat-Menard, 1986; Liss and Slater, 1974).

Deposition velocity can be estimated by a number of direct and indirect techniques. Direct methods entail physically measuring the vertical flux of a gas to or near the surface, which usually requires the use of sophisticated equipment. Examples of these types of techniques include (Seinfeld and Pandis, 1998; Shahin et al., 1999; Shahin et al, 2002):
- **Chamber Method** - In open or closed chambers, the factors thought to influence gas deposition are controlled while gas uptake by the surface is measured over a prescribed period of time.

- **Eddy Correlation** – A micrometeorological technique involving rapid measurements of vertical wind velocity $w'(t)$ and concentration $C'(t)$ to obtain a time series of the fluctuating component. Data are then averaged to obtain the vertical turbulent flux of the chemical of interest ($F = \overline{w'C'}$). Deposition velocity is obtained by dividing the measured flux by the average concentration at a specific reference height.

- **Surrogate or Natural Surfaces** – Dry deposition rates are determined by measuring the mass accumulation of a chemical species to a surface over a specified period of time. This technique is relatively ineffective for gases, except for soluble species’ deposition to a water surface.

Indirect methods determine flux values by measurements of secondary quantities, such as heat, moisture or momentum, and associating these values with those of the gas of interest (Valigura, 1995), an assumption supported by field studies of the atmospheric transport of ozone and carbon dioxide (Hicks and Liss, 1976). Examples of these types of techniques include (Seinfeld and Pandis, 1998):

- **Gradient Method** – The deposition velocity is determined by measuring the vertical gradient of the depositing gas and using
gradient-transport or bulk-transport theory to infer the associated flux. This method requires that accurate concentration measurements be made at two or more heights in the mixed layer.

- **Inferential Method** - Measured ambient gas concentrations are multiplied by a deposition velocity assumed to be representative of the surface characteristics to obtain the flux rate for the species of interest.

4.1.1.1 The NOAA Buoy Model

The NOAA Buoy model was developed by R.A. Valigura of the NOAA Air Resources Laboratory as a tool for estimating the air-water exchange rates (deposition velocities) of nitric acid (HNO$_3$) over coastal water bodies (Valigura, 1995). The model is available for use at http://www.eng.usf.edu/~bhethana/.

Model development included the use of near-surface, over-water coastal meteorological data obtained from a network of buoys to simulate existing small-scale coastal conditions. Given that the model was developed for nitric acid, which is very soluble and usually present in relatively high ambient concentrations in coastal areas, transfer was considered unidirectional. Additional assumptions were that surface and quasi-laminar resistances are negligible compared to aerodynamic resistance, and therefore were not considered during formulation of the model (Valigura, 1995). A major assumption in the model is that nitric acid gas and sensible heat are similarly regulated by aerodynamic resistance (Hicks and Liss, 1976). Therefore, the dimensionless heat transfer coefficient ($D_H$), estimated with the general bulk
transfer equations, was used to estimate the deposition velocity of HNO$_3$ as follows:

$$v_d = r_{a,H}^{-1} = D_H u_z$$

(Equation 4.3)

where $r_a$ is the aerodynamic resistance for heat, $D_H$ is the dimensionless heat transfer coefficient, and $u_z$ is the measured wind speed at height $z$ in m s$^{-1}$.

The model was formulated based on the works of Hicks (1975), Hicks and Liss (1976), and Liu and Schwab (1987) and entails the use of both the bulk exchange method and the flux-gradient relationships as follows:

- The bulk transfer coefficient equations determine turbulent fluxes for heat ($H$), moisture ($LE$), and momentum ($\tau$) (Hicks, 1975):

$$H = \rho c_p D_H u_z (T_o - T_z)$$

(Equation 4.4)

$$LE = \rho L_W D_W u_z (q_o - q_z)$$

(Equation 4.5)

$$\tau = \rho C_d u_z^2$$

(Equation 4.6)

where $T$ is temperature, $q$ is specific humidity, and $u$ is wind speed at the respective measurement heights at the surface ($0$) and at a chosen elevation ($z$), $\rho$ is air density, $L_W$ is the latent heat of vaporization, $c_p$ is the specific heat of air, $C_d$ is the drag coefficient, and $D_H$ and $D_W$ are the transfer coefficients for heat and water, respectively.
The flux-gradient relationships were then derived by integrating the bulk transfer coefficient equations from the surface to measurement height \( z \) (Hicks, 1975):

\[
T_o - T_z = \left( \frac{H}{\rho c_p k u} \right) \ln \left( \frac{z}{z_H} \right) - \psi_H \left( \frac{z}{L} \right) \quad \text{(Equation 4.7)}
\]

\[
q_o - q_z = \left( \frac{E}{\rho k u_*} \right) \ln \left( \frac{z}{z_w} \right) - \psi_w \left( \frac{z}{L} \right) \quad \text{(Equation 4.8)}
\]

\[
u_z - u_o = \left( \frac{u_*}{k} \right) \ln \left( \frac{z}{z_0} \right) - \psi_M \left( \frac{z}{L} \right) \quad \text{(Equation 4.9)}
\]

where Panofsky’s \( \psi \) functions allow atmospheric stability effects to be incorporated into the flux-gradient relationships, \( L \) is the Obukhov length scale which describes the layer of dynamic influence near the surface where shear or friction effects are always important, \( E \) is the moisture flux, \( k \) is the von Karman’s constant (defined as 0.4), \( u_* \) is the friction velocity, and \( z_H, z_w, \) and \( z_0 \) are roughness lengths for heat, moisture, and momentum transport, respectively, which describe the rate of uptake of these parameters at the surface (Hicks, 1975). Based on the above relationships, expressions for the dimensionless transfer and drag coefficients were derived as follows:
Inputs to the model include hourly wind speed, wind direction, air and water temperature, and relative humidity. Before the model begins iteration, equations are used to account for the difference between the surface and subsurface water temperatures, caused by the formation of a “thermal skin” at the water surface. This thin layer forms due to the loss or gain of heat through evaporation, sensible heat transfer, and back radiation and is also dependent on the wind speed and shortwave radiation (Hasse, 1971). After accounting for this difference, the model begins iteration with an initial approximation of the transfer coefficients until the modeled temperature and wind gradients match the measured wind speed and temperature differentials (Valigura, 1995). At this point the modeled hourly transfer coefficient for heat and the measured wind speed are used to calculate the deposition velocity, as shown in Equation 4.3. Once deposition velocities are determined from the model, the inferential technique is used to calculate the flux rates as described in section 4.1.1.
4.1.1.2 Model Improvements

The NOAA Buoy model is an effective tool for estimating the air-water exchange rates of important atmospheric gases. The model is used extensively to determine the deposition velocities of gases over Tampa Bay, however, there are limitations that must be addressed. The model was developed using over-water meteorological instruments to measure input parameters. Often, only near-shore measurements are available, due to the long-term costs of operating and maintaining buoys for these measurements. These input measurements may not accurately predict over-water flux parameters due to different meteorological conditions typically found over land. In addition, the model was originally developed to determine nitric acid exchange rates, which are usually unidirectional due to the relatively high ambient air concentrations of this gas. But this assumption does not apply to ammonia exchange, which may be bi-directional during the summer months when bay water ammonium concentrations are elevated (Poor et al., 2001). The goals of this study are to improve the NOAA Buoy model for ammonia flux calculations by determining correction factors for the near-shore meteorological measurements and including algorithms for bi-directional flux estimates.

4.1.2 Bi-directional Flux Analysis

The detrimental effects of ammonia enrichment on land and water bodies are widely known and numerous quantitative studies have been and are in the process of being conducted to determine these effects. Dry deposition studies
over land have been performed to determine the effects of ammonia on forests, vegetation, and soil. Langford and Fehsenheld (1992) conducted research above a subalpine forest in Colorado to determine if the forest was a source or sink of ammonia. They discovered that when atmospheric concentrations are generally low and representative of background conditions, the forest acts as a source of ammonia. However, when the air is enriched by nearby agricultural sources, the forest acts as a sink. This trend is also seen with bi-directional surface exchange of ammonia over semi-vegetated land, most notably over wheat fields in England. Sutton et al. (1998) found that the main processes regulating bi-directional ammonia fluxes over these fields are plant cuticular and leaf tissue exchange, which are regulated by temperature, moisture, plant phenology, and ambient air ammonia concentrations. Regardless of the land cover, the bi-directional flux of ammonia over land is modeled with the use of a compensation point, which is the concentration in the ambient air that is in equilibrium with the plant tissue or soil (Farquhar et al., 1980; Flechard et al., 1999). When the ambient air concentration is not equal to the compensation point, a negative or positive flux will occur (Yamulki et al., 1996).

Recent research has suggested that the ammonia flux is also consistently bi-directional over water bodies, and the principle determinants of the direction of flux are the airborne and water concentrations of ammonia (Asman et al., 1994; Genfa et al., 1998; Pryor et al., 1999; Quinn et al., 1996). Research conducted in coastal waters of the northeast Pacific Ocean found that for the region and time period studied (May 1987), the ocean was a local source of atmospheric
ammonia and it was conserved as it cycled through the marine environment (Quinn et al., 1992). Likewise, Asman et al. (1994) used an equilibrium model to calculate the direction of the ammonia flux over the North Sea. They found that the net ammonia flux was from the air to the sea for the majority of their samples. However, the North Sea acted as a source of atmospheric ammonia during the summer months, coincident with an increase in ambient water concentrations of ammonium in a local estuary. They also discovered that elevated air and water concentrations occurred closer to the coasts due to the abundance of land-based and estuarine sources. Similar findings in the North Sea by Barrett (1998), Lee et al. (1998), and Sorensen et al. (2003) suggest that ammonia deposition is dominant in this water body, but that the high marine source strength along the coastline often contributes to ammonia emissions from the water to the air. Likewise, in the Baltic Sea, mean monthly emissions of ammonia from the water were highest from July through September (Barrett, 1998). Barrett (1998) also suggests that ammonia is cycled internally and re-deposited in the marine environment and that modeled marine ammonia emissions are similar in magnitude to small Northern European countries. Research conducted in the Chesapeake Bay found that the ammonia flux is bi-directional, greater, and more variable in urban Baltimore than a rural research site in Maryland (Larsen et al., 2001). The air-sea exchange flux varied seasonally from a net deposition into the water during the winter to a net volatilization into the atmosphere during the summer due to an increase in bay water concentrations of ammonia, pH and temperature.
4.2 Objectives and Hypotheses

The objectives of this research are to evaluate the NOAA Buoy model as a tool for estimating the air/water exchange rates of ammonia to Tampa Bay and to alter the model for bi-directional flux estimates. The following research questions and hypotheses will be addressed in this chapter:

- How well does the NOAA Buoy model predict heat transfer and the resulting air/water exchange rates of soluble gases over Tampa Bay?
  - *Hypothesis 1*: The model accurately predicts transfer properties when input parameters are measured over coastal waters (Valigura, 1995).
  - *Hypothesis 2*: Due to the effects of differing meteorological conditions over land, the model under-predicts transfer rates when input parameters are measured near the shoreline.

- Are predicted ammonia flux estimates bi-directional in the summer season?
  - *Hypothesis 3*: Ammonia flux rates are bi-directional in the summer months when marine conditions are optimal and biological activity is increased (Poor et al., 2001). An algorithm developed by Asman et al. (1994) can be integrated into the NOAA Buoy model to predict this activity.
4.3 Study Locations and Duration

4.3.1 Model Evaluation and Improvement

Offshore model evaluation occurred at the Port Manatee Turn meteorological tower from June - November 2002. The model was not evaluated from December 2002 through May 2003 because water temperature data was not available for this time period. Near-shore measurements and model evaluation occurred at the Picnic Island Pier during November 2002 and at the Gandy Bridge site from June - August 2003.

4.3.2 Bi-directional Flux Analysis

Daily water samples and 12-hour integrated air samples were collected at the Picnic Island Pier for two monitoring periods: November 3-18, 2002 and January 18-February 2, 2003. Due to security concerns, samples were no longer collected at the Picnic Island Pier and daily water and 24-hour integrated air sampling was established at the Gandy Bridge site from June 10-August 21, 2003. For consistent comparisons with Gandy Bridge data, the mass quantities of the 12-hour integrated diurnal samples collected at Picnic Island Pier were combined to provide average 24-hour integrated air and water samples.
4.4 Sample Collection and Analysis

4.4.1 Model Evaluation

4.4.1.1 Port Manatee Turn

Meteorological and eddy correlation measurements of heat, moisture and momentum were made at the Port Manatee Turn BRACE meteorological tower, as described in Chapter 1. Sensible heat measurements were made with the CSAT3, a three-dimensional sonic anemometer manufactured by Campbell Scientific, which measures wind speed and the speed of sound on three non-orthogonal axes at 6.92-m above mean sea level (MSL). The wind speeds were transformed into the orthogonal wind components $u_x$, $u_y$, and $u_z$ and referenced to the anemometer head. The vertical fluxes of momentum, sensible heat and water vapor, $F = \rho u' w'$, $H = \rho c_p \theta' w'$ and $E = \rho q' w'$, were calculated as the product of instantaneous scalars and averaged over 30 minute time periods. Sensible heat data from the top of each hour were utilized for analysis in this study.

Meteorological measurements made at the site included hourly horizontal wind speed and direction, air temperature, and relative humidity at 5-m and 10-m above the MSL, and water temperature at 2-m below the MSL. The air temperature/relative humidity and wind monitor instruments were manufactured by R.M. Young and the water temperature gauge was manufactured by Sea-Bird Electronics. Meteorological measurements were made and the data downloaded via line-of-sight radio every six minutes. Wind speed and direction measured at 10-m above the MSL, air temperature and relative humidity measured at 5-m
above the MSL, and water temperature data from the top of each hour were utilized for this study. The 5-m and 10-m data were used for consistency with near-shore meteorological input measurements made at 6-m and 10-m above the water surface at the Gandy Bridge and Picnic Island sites.

Data from the array were telemetered continuously by line-of-sight radio to the Ocean Modeling and Prediction Lab in the USF College of Marine Science. Data are available in real-time via the Web and are archived in a searchable database (see http://comps.marine.usf.edu/BRACE/).

Meteorological measurements made at the tower were used as inputs to the model, and the modeled sensible heat fluxes were compared with the actual measurements of sensible heat flux made with the CSAT3 sonic anemometer to determine how well the NOAA Buoy model predicts flux parameters at an offshore coastal site in Tampa Bay.

4.4.1.2 Picnic Island

Meteorological measurements made at the site included hourly air temperature and relative humidity at 1-m and 6-m above the MSL, wind speed and direction at 10-m above the MSL, and water temperature at 1-m below the MSL. The wind monitor instrument was manufactured by R.M. Young and the air temperature and relative humidity probes were manufactured by Omega, Inc. The minisonde water gauge, which monitored hourly water temperature, pH, and salinity, was manufactured by HydroLab, Inc. Wind speed and direction data were downloaded via line-of-sight radio to the Ocean Modeling and Prediction Lab in the USF College of Marine Science. Data are available in real-time via the
Web (see http://ompl.marine.usf.edu/PORTS/g8726607.html). The air and relative humidity probes and the minisonde water gauge were programmed, calibrated, and downloaded at the University of South Florida, College of Public Health Environmental Laboratory.

Meteorological measurements were used as inputs to the NOAA Buoy model, and the modeled sensible heat fluxes were compared with the actual measurements of sensible heat flux made at the offshore Port Manatee Turn BRACE tower for the same time period to determine how well the NOAA Buoy model predicts flux parameters at a near-shore coastal site in Tampa Bay.

4.4.1.3 Gandy Bridge

Meteorological measurements made at the site included hourly air temperature and relative humidity at 1-m and 6-m above the MSL, wind speed and direction at 10-m above the MSL, and water temperature at 1-m below the MSL. The wind monitor instrument was manufactured by R.M. Young and the air temperature and relative humidity probes were manufactured by Omega, Inc. The minisonde water gauge, which monitored hourly water temperature, pH, and salinity, was manufactured by HydroLab, Inc. Wind speed and direction data were obtained from the Environmental Protection Commission of Hillsborough County. The air and relative humidity probes and the minisonde water gauge were programmed, calibrated, and downloaded at the University of South Florida (USF), College of Public Health Environmental Laboratory.

Meteorological measurements were used as inputs to the NOAA Buoy model, and the modeled sensible heat fluxes were compared with the actual
measurements of sensible heat flux made at the offshore Port Manatee Turn tower for the same time period to determine how well the NOAA Buoy model predicts flux parameters at a near-shore coastal site in Tampa Bay.

4.4.2 Bi-directional Flux Analysis

4.4.2.1 Air Concentrations

During the Picnic Island Pier and Gandy Bridge monitoring events, ambient air concentrations of gaseous ammonia were measured at 6-m above Tampa Bay with a dual pump, URG, Inc., annular denuder system (ADS), as described in Chapter 2.

At the Picnic Island Pier, the annular denuder was located on a utility pole at the end of the pier and housed in a specially constructed PVC container. The annular denuder was attached to the light pole and was raised and lowered as needed with a pulley. The pump operated at an airflow of 10 L min\(^{-1}\) for approximately 12 hours at a time. Each ADS consisted of a 2.5-µm particle aerodynamic diameter cut-point Teflon coated cyclone inlet and two 150-mm long gas denuders connected in series and coated with phosphoric acid to absorb ammonia.

At the Gandy Bridge site, air measurements were made on a seawall located adjacent to Tampa Bay. In addition to the 6-m measurements, air concentrations were measured at 1-m as well. The annular denuders were housed in specially constructed PVC containers. The annular denuder at 1-m above the MSL was attached to a rope at the seawall and the annular denuder at
6-m was attached to a 6-m telescoping flagpole that was raised and lowered as needed. The pump operated at an airflow of 20 L min\(^{-1}\) for approximately 24-hours at a time. Each ADS consisted of a 2.5 \(\mu\)m particle aerodynamic diameter cut-point Teflon coated cyclone inlet and two 150-mm long gas denuders connected in series and coated with phosphoric acid to absorb gaseous ammonia.

The annular denuder samples were prepared, extracted, and analyzed at the University of South Florida (USF), College of Public Health Environmental Laboratory. Denuders were prepared as described in Chapter 2. The denuder extracts were analyzed for ammonium by ion chromatography and all samples were stored in 10-ml Dionex vials and refrigerated until analysis.

### 4.4.2.2 Bay Water Concentrations

For each measurement period at the Picnic Island Pier and Gandy Bridge sites, water samples were collected at the surface of the bay to determine the ammonium concentrations. Sampling was conducted with a multi-depth water sampler manufactured by Aquatic Research Instruments, Inc. Upon collection with the sampler, the sample bottle was first rinsed twice with sample water prior to sample collection. Samples were immediately delivered to the Environmental Protection Commission of Hillsborough County’s Water Management Laboratory where they were acidified to pH<2 to prevent chemical and biological transformations and analyzed by automated colorimetry for ammonium. All samples were stored refrigerated and analyzed in accordance with the
specifications in Part 4500-NH$_3$ of “Standard Methods for the Examination of Water and Wastewater” (Clesceri et al., 1998).

Bay water ammonium concentration data were smoothed by taking a simple moving average of each sample obtained at the beginning and end of each denuder measurement period. This technique was employed to more accurately represent the ammonium concentrations over the 24-hour sampling intervals. The equilibrium air concentration of ammonia (C$_{eq}$), which is the ammonia concentration in air that is in equilibrium with the ammonium concentration in the bay water, was calculated for each sample based on the average bay water ammonium concentration.

4.4.2.3 Flux Calculations

Hourly modeled deposition velocities were averaged over each measurement period and used to calculate the ammonia flux as follows:

$$F_{dry} = (C_{air} - C_{eq}) v_d t$$

(Equation 4.13)

where $F_{dry}$ is the dry flux of ammonia at the air/water interface (µg-NH$_3$ m$^{-2}$ day$^{-1}$), $C_{air}$ is the 24-hour integrated air concentration of ammonia measured at 6-m (µg m$^{-3}$), $C_{eq}$ is the equilibrium air concentration of ammonia (µg m$^{-3}$), $v_d$ is the NOAA Buoy modeled deposition velocity (m s$^{-1}$), and $t$ is the sampling time (s).
The equilibrium air concentration was calculated as (Asman et al., 1994):

\[
C_{eq} = \frac{M_{NH3}[NH_x]}{RTH_{NH3}} \left( \frac{1 + 10^{-\rho pH}}{\gamma_{NH3} \gamma_{NH4} K_{NH4}} \right)
\]  

(Equation 4.14)

where \(M_{NH3}\) is the molecular mass of \(NH_3\) (g mol\(^{-1}\)), \([NH_x]\) is the \(NH_x\) concentration in seawater at the water surface (\(\mu M\)), \(\gamma_{NH3}\) is the activity coefficient of \(NH_3\cdot H_2O\), \(\gamma_{NH4}\) is the activity coefficient of \(NH_4^{+}\) in seawater, \(R\) is the gas constant (8.2075 x 10\(^{-5}\) atm m\(^3\) mol\(^{-1}\) K\(^{-1}\)), \(T\) is the water temperature (Kelvin), \(H_{NH3}\) is the Henry’s law constant for \(NH_3\) (M atm\(^{-1}\)), \(\rho pH\) is the pH of seawater, and \(K_{NH4}\) is the dissociation constant for \(NH_4^{+}\) (M). This equation determines the aqueous-phase partitioning of ammonia and ammonium and the equilibrium between aqueous and gas-phase ammonia as predicted by Henry’s Law (Larsen et al., 2001; Pryor and Sorensen, 2002; Sorensen et al., 2003).

The temperature dependent Henry’s law (Dasgupta and Dong, 1986) and dissociation constants (Bates and Pinching, 1950) were calculated with the following equations,

\[
H_{NH3} = 56 \exp\left(4092\left(1 - \frac{1}{T - 298.15}\right)\right)
\]  

(Equation 4.15)

\[
K_{NH4} = 5.67 \times 10^{-10} \exp\left(-6286\left(1 - \frac{1}{T - 298.15}\right)\right)
\]  

(Equation 4.16)
The activity coefficients for ammonia (Garrels and Christ, 1965) and ammonium (Millero and Schreiber, 1982) in seawater are,

\[ \gamma_{NH_3} = 1 + 0.08I \]  
(Equation 4.17)

\[ \gamma_{NH_4} = 0.883 - 0.0768 \ln S \]  
(Equation 4.18)

where \( I \) is the ionic strength for seawater (Lyman and Fleming, 1940) as a function of salinity, \( S (\text{‰}) \),

\[ I = 0.00147 + 0.01988S + 2.08357 \times 10^{-5} S^2 \]  
(Equation 4.19)

The flux (Equation 4.13) is positive when ammonia is deposited to the bay \( (C_{\text{air}} > C_{\text{eq}}) \) and negative when the equilibrium concentration is greater than the ambient air concentration of ammonia.

4.5 Quality Assurance/Quality Control

4.5.1 Port Manatee Turn

A data acquisition, archival, and distribution system that includes a database-driven web site to provide on-line access to all relevant data collected under this program was developed by the Ocean Modeling and Prediction Lab in the USF College of Marine Science. Also available is a Web-based front end with a database back end to make all the data and metadata accessible to the
visitors of the web site. Users are able to search the database using web-based forms, to generate results, and to download data. Real-time graphics are generated from the data using IDL and MATLAB scripts and all data are archived in a MySQL-compliant searchable database. All raw data and FGDC-compliant metadata are maintained in a permanent archive. Routine back-ups are produced to guard against any data loss and a data administration system provides continuous evidence of data possession and control with signatures, dates, times, and location of data being noted. An automated Quality Assurance/Quality Control (QA/QC) procedure was developed for all data acquired under this task.

All instruments were certified calibrated by the respective manufacturers and certificates are available at the COMPS website (ftp://comps.marine.usf.edu/pub/BRACE/seagauge_data/instr/). Instruments were operated, maintained, and serviced according to the manufacturers specifications by the Ocean Modeling and Prediction Lab in the USF College of Marine Science.

For both the measured and modeled datasets, data points outside of the 90% confidence interval were considered outliers and removed prior to data analysis and comparison.
4.5.2 Gandy Bridge and Picnic Island Pier

4.5.2.1 Air Measurements

Wind monitors at the Picnic Island Pier and Gandy Bridge sites were operated, maintained and serviced according to the manufacturers specifications by the Ocean Modeling and Prediction Lab in the USF College of Marine Science and the Environmental Protection Commission of Hillsborough County, respectively.

The air temperature and relative humidity probes were certified calibrated by the manufacturer. QA/QC measures for denuders were described in Chapter 2.

4.5.2.2 Water Measurements

The Hydrolab minisonde water monitor, deployed for no longer than 5 days at a time, was operated, maintained and serviced according to the manufacturers specifications, which included calibration prior to and following each deployment. Upon return to the laboratory for calibration, the water quality information, which included hourly temperature, pH, and salinity measurements, was downloaded to a computer and saved for future analysis. The next sampling cycle was then programmed and the instrument was returned to the field for data collection following calibration.

Bay water sample bottles were labeled with the collection date. Following analysis, bottles were washed thoroughly with >18 MΩ deionized water. Weekly field blanks ranged from between 10% to 100% of the sample concentrations,
and blank values were subtracted from the sample concentrations for future analysis.

Bias in the bay water samples was likely present because samples were obtained at the beginning and end of each denuder sampling interval. To reduce uncertainty inferred in the 24-hour averaged estimates, a simple moving average was calculated to provide a better representation of the average concentrations. Cost constraints prevented sample collection at greater resolution. It is recommended that for future studies of bay water ammonium concentrations, hourly or bi-hourly measurements be made to determine a more precise diurnal average of ammonium.

4.6 Results and Discussion

4.6.1 Model Evaluation

4.6.1.1 Offshore Measurements

Measured and modeled intercomparisons of sensible heat flux (H) at the Port Manatee Turn meteorological tower from June - November 2002 are shown: 1) collectively in Figures 4.1 and 4.2; and 2) monthly in Figures 4.3 - 4.8. The NOAA Buoy model estimated H well with an overall $R^2$ value of 0.86 and an average mean difference of 4.4 W m$^{-2}$. In Table 4.1 is shown the summary statistics for the measured and modeled intercomparisons of sensible heat flux. A paired, two-tailed t-test on the set of 3,674 data points, however, resulted in a statistically significant difference between measured and modeled values ($p=3.8 \times 10^{-17}$).
On a monthly basis, the model slightly under-predicts the measured values during the months of June, July, August, and September, with a mean $R^2$ value of 0.78. The model's predictive ability became progressively improved during the months of October and November, with a mean $R^2$ value of 0.90. This seasonal imparity may be the result of a vertical temperature gradient caused by a difference in height of 1.92-m between the CSAT3 sonic anemometer (6.92-m) and the temperature sensor (5.0-m). In addition, the sonic anemometer contains a sun shield, while the R.M. Young meteorological sensor does not. Based on the results of this analysis, it is well represented that the NOAA Buoy model accurately predicts over-water heat flux in the Tampa Bay estuary.
Figure 4.1 Modeled and Measured Sensible Heat Flux at the Port Manatee Turn Meteorological Tower, June - November, 2002

Figure 4.2 Scatter Plot of Modeled and Measured Sensible Heat Flux at the Port Manatee Turn Meteorological Tower, June - November, 2002

June - November 2002

\[ y = 0.79x + 7.92 \]

\[ R^2 = 0.86 \]
Figure 4.3 Scatter Plot of Modeled and Measured Sensible Heat Flux at the Port Manatee Turn Meteorological Tower, June 2002

June 2002

\[ y = 0.70x + 10.41 \]

\[ R^2 = 0.78 \]

Figure 4.4 Scatter Plot of Modeled and Measured Sensible Heat Flux at the Port Manatee Turn Meteorological Tower, July 2002

July 2002

\[ y = 0.67x + 11.67 \]

\[ R^2 = 0.79 \]
Figure 4.5 Scatter Plot of Modeled and Measured Sensible Heat Flux at the Port Manatee Turn Meteorological Tower, August 2002

August 2002

$y = 0.65x + 11.92$

$R^2 = 0.79$

Figure 4.6 Scatter Plot of Modeled and Measured Sensible Heat Flux at the Port Manatee Turn Meteorological Tower, September 2002

September 2002

$y = 0.65x + 8.06$

$R^2 = 0.75$
Figure 4.7 Scatter Plot of Modeled and Measured Sensible Heat Flux at the Port Manatee Turn Meteorological Tower, October 2002

\[
y = 0.81x + 7.06 \\
R^2 = 0.83
\]

Figure 4.8 Scatter Plot of Modeled and Measured Sensible Heat Flux at the Port Manatee Turn Meteorological Tower, November 2002

\[
y = 0.90x + 3.84 \\
R^2 = 0.95
\]
Table 4.1 Summary Statistics of Measured and Modeled Sensible Heat Flux at Port Manatee Turn Meteorological Tower, June - November, 2002 (W m\(^{-2}\))

<table>
<thead>
<tr>
<th>Data</th>
<th>Mean</th>
<th>Median</th>
<th>Standard Deviation</th>
<th>n</th>
<th>p</th>
<th>Average Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
<td>21.6</td>
<td>17.2</td>
<td>20.1</td>
<td>3674</td>
<td>3.8\times10^{-17}</td>
<td>4.4</td>
</tr>
<tr>
<td>Modeled</td>
<td>17.2</td>
<td>12.2</td>
<td>23.5</td>
<td>3674</td>
<td>4.4</td>
<td></td>
</tr>
</tbody>
</table>
4.6.1.2 Near-shore Measurements

Near-shore and offshore modeled flux parameters were compared for the November 3 - 18, 2002, and June 28 - August 22, 2003 modeling periods to determine if the NOAA Buoy model accurately predicts over-water flux parameters when meteorological measurements are made near-shore.

For the November 3 - 18, 2002 measurement comparison between the Picnic Island Pier and Port Manatee Turn meteorological tower, the model predicted well the sensible heat flux, with an $R^2$ value of 0.85 (Figures 4.9 and 4.10) and a mean difference of 8.8 W m$^{-2}$ (Table 4.2). An experimental verification of the bulk transfer equation for heat ($H = \rho c_p \Delta T \frac{D_H u_z}{z}$; Equation 4.4) is presented in Figures 4.11 and 4.12, in which the near-shore and offshore vertical flux of sensible heat is shown to be well correlated with the product of wind speed and the modeled air/water temperature differential. The dimensionless heat transfer coefficient ($D_H$), given by the slope of the regression line, is $1.3 \times 10^{-3}$ for both the near-shore and offshore sampling periods. This value is consistent with those given by Arya (1988), who provides typical values for comparatively smooth water surfaces of between $1.0 \times 10^{-3}$ and $2.0 \times 10^{-3}$. Comparison of near-shore and offshore hourly winds also resulted in average values of 5.0 m s$^{-1}$ for both (Table 4.2). A paired, two-tailed t-test on the set of 240 data points resulted in a statistically significant difference between measured and modeled values ($p=8.6\times10^{-3}$).
The same comparison was made for the summer season at the Gandy Bridge monitoring site and the Port Manatee Turn meteorological tower. The model did not perform as well, significantly under-predicting the sensible heat flux by 56%, with an $R^2$ value of 0.34 (Figures 4.13 and 4.14; Table 4.2). A comparison of the dimensionless heat transfer coefficients shows that the near-shore modeled value of $1.0 \times 10^{-3}$ is almost 30% lower than the offshore value of $1.4 \times 10^{-3}$ (Figures 4.15 and 4.16). This was caused by a substantially lower average temperature differential between the water surface and the air above it, with more negative differentials near-shore than offshore, as shown in Figure 4.17 and Table 4.2. Comparison of winds resulted in a 33% lower average wind speed near-shore than offshore (Table 4.2). A paired, two-tailed t-test on the set of 871 data points resulted in a statistically significant difference between measured and modeled values ($p=1.0\times10^{-18}$).

These disparities are a result of the difference in surface temperatures between the land and water. As distinguished from land surfaces, water bodies are characterized by a notable spatial and temporal homogeneity of temperature, which is due to the large heat capacity and efficient mixing processes in the upper mixed layer of the water body (Arya, 1988). In the summer season when air and water temperatures are at their maximum, water bodies are able to store and retain incoming radiation more efficiently than land surfaces, resulting in a small diurnal range in sea surface temperature. Near the shoreline adjacent to the seawall, however, air measurements were made at 10 meters above and water measurements at 2 meters below the water surface. Thus due to the close
proximity to land, it is possible that the elevated air temperatures resulted in inversions at the shoreline, compared to temperature differentials measured offshore. The increased frequency of near-shore negative temperature differentials resulted in reduced turbulence and an underestimation of heat transfer between the water and air, which also resulted in a biased prediction of gas-phase mass transfer over coastal waters.

Based on the results of this study, it was discovered that the NOAA Buoy model underestimates over-water flux parameters during the summer season when near-shore meteorological measurements are used as inputs to the model. However, the model more accurately predicts over-water flux parameters with near-shore meteorological measurements during the fall season, when air/water temperature differentials are consistently positive throughout the estuary and wind speeds are higher as a result of cool ambient air temperatures. Due to the climate in the region, this theory likely applies to the winter season as well, in which near-shore meteorological measurements accurately predict over water flux parameters.
Figure 4.9 Modeled Near-shore and Measured Offshore Sensible Heat Flux, November 3 - 18, 2002

Figure 4.10 Scatter Plot of Modeled Near-shore and Measured Offshore Sensible Heat Flux, November 3 - 18, 2002

$y = 1.06x + 15.10$

$R^2 = 0.85$
Figure 4.11 Sensible Heat Flux at the Bay Surface as a Function of Near-shore \(u(T_o-T_a)\)  
(Equation 4.4) with \(D_H = 1.3 \times 10^{-3}\), November 3 - 18, 2002

\[
y = 1.3E-03x + 0.0082
\]

\[
R^2 = 0.95
\]

Figure 4.12 Sensible Heat Flux at the Bay Surface as a Function of Offshore \(u(T_o-T_a)\)  
(Equation 4.4) with \(D_H = 1.3 \times 10^{-3}\), November 3 - 18, 2002

\[
y = 1.3E-03x + 0.0058
\]

\[
R^2 = 0.96
\]
Figure 4.13 Modeled Near-shore and Measured Offshore Sensible Heat Flux, June 9 - August 22, 2003

Figure 4.14 Scatter Plot of Modeled Near-shore and Measured Offshore Sensible Heat Flux, June 9 - August 22, 2003

\[ y = 0.55x + 17.95 \]

\[ R^2 = 0.34 \]
Figure 4.15 Sensible Heat Flux at the Bay Surface as a Function of Near-shore $u(T_o-T_a)$ (Equation 4.4) with $D_H = 1.0 \times 10^{-3}$, June 28 - August 22, 2003

$$y = 9.8E-04x + 0.0054$$
$$R^2 = 0.84$$

Figure 4.16 Sensible Heat Flux at the Bay Surface as a Function of Offshore $u(T_o-T_a)$ (Equation 4.4) with $D_H = 1.4 \times 10^{-3}$, June 28 - August 22, 2003

$$y = 1.4E-03x + 0.0016$$
$$R^2 = 0.97$$
Figure 4.17 Hourly Air and Water Temperature Differences, June 28 - August 22, 2003

Table 4.2 Near-shore and Offshore Flux Parameters

<table>
<thead>
<tr>
<th>Modeled Results</th>
<th>Mean Sensible Heat Flux (W m(^{-2}))</th>
<th>Mean (T_{\text{surface}} - T_{\text{air}}) (°C)</th>
<th>Mean WS (m s(^{-1}))</th>
<th>Mean Deposition Velocity (m s(^{-1}))</th>
<th>n</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>November 3-18, 2002</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Near-shore</td>
<td>24.5</td>
<td>0.7</td>
<td>5.0</td>
<td>7.4 x 10(^{-3})</td>
<td>240</td>
<td>8.6x10(^{-3})</td>
</tr>
<tr>
<td>Offshore</td>
<td>33.3</td>
<td>1.4</td>
<td>5.0</td>
<td>8.7 x 10(^{-3})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>June 28 - August 22, 2003</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Near-shore</td>
<td>6.5</td>
<td>0.01</td>
<td>2.6</td>
<td>4.3 x 10(^{-3})</td>
<td>871</td>
<td>1.0x10(^{-18})</td>
</tr>
<tr>
<td>Offshore</td>
<td>14.6</td>
<td>1.6</td>
<td>3.8</td>
<td>6.6 x 10(^{-3})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.6.2 Model Improvement

To “calibrate” the NOAA Buoy model in the summer season, large negative near-shore temperature differentials were removed from the dataset until the slope of the regression line (Figure 4.15; $D_H=1.0 \times 10^{-3}$) was increased to the slope of the offshore model (Figure 4.16; $D_H=1.4 \times 10^{-3}$). As shown in Figures 4.16 and 4.18, when modeled near-shore temperature differentials less than -4.8 were removed from the dataset, the slope was increased to $D_H=1.4 \times 10^{-3}$. The removed variables accounted for 20% of the original near-shore dataset and all occurred in the daytime between the hours of 10:00 and 20:00.

Based on the results of this study, it is recommended that when utilizing the NOAA Buoy model for prediction of gas-phase mass transfer during the summer season with near-shore meteorological input measurements, hourly modeled results with a temperature differential less than -4.8 be removed from the dataset prior to use to prevent a biased under-prediction of over-water flux parameters during the daytime hours.
Figure 4.18 Result of Model Calibration of Near-shore Heat Flux with $D_h = 1.4 \times 10^{-3}$, June 28 - August 22, 2003 (Temperature Differentials Less than -4.8 were Removed from the Dataset)

$y = 1.4E-03x + 0.0031$

$R^2 = 0.92$
4.6.3 Bi-directional Flux Analysis

The 24-hour averaged ammonia flux rates (Equation 4.13) are depicted in Figure 4.19. The modeled results indicate that during the November 2002 and January 2003 measurement periods at the Picnic Island Pier, the average ammonia flux rate was positive, indicating deposition to Tampa Bay a majority of the time. The average ammonia flux rates for November 2002 and January 2003 were 54.9 µg-NH$_3$ m$^{-2}$ d$^{-1}$ and 137.4 µg-NH$_3$ m$^{-2}$ d$^{-1}$, respectively (Table 4.3). During the Summer 2003 (June 28 - August 22, 2003) measurement period at the Gandy Bridge monitoring site, the average "calibrated" ammonia flux rate was from the bay to the atmosphere, at -117.9 µg-NH$_3$ m$^{-2}$ d$^{-1}$ (Table 4.3). This indicates that Tampa Bay acts as a source of atmospheric ammonia during the summer months, results consistent with those of Asman et al. (1994), Barrett (1998), Larsen et al. (2001), Lee et al. (1998), and Poor et al. (2001). These rates are lower than those measured by Larsen et al. (2001), who found ammonia flux rates in the Chesapeake Bay estuary ranging from an extreme net volatilization of -2900 µg-N m$^{-2}$ d$^{-1}$ to a net deposition of 1200 µg-N m$^{-2}$ d$^{-1}$. Asman et al. (1994) found ammonia flux rates in the North Sea ranging from a net volatilization of -602 µg-N m$^{-2}$ d$^{-1}$ to a net deposition of 1050 µg-N m$^{-2}$ d$^{-1}$, which is consistent with these findings.

Modeled flux rates are dependent on air and bay water equilibrium concentrations. During the November 2002, January 2003, and Summer 2003 sampling periods, the average air concentrations of ammonia did not vary significantly, ranging from 0.84 to 1.93 µg m$^{-3}$ (Table 4.4). However, the bay
water equilibrium ammonia concentrations did vary considerably by season, ranging from a low of 0.23 µg m\(^{-3}\) in January to a high of 2.76 µg m\(^{-3}\) during the summer season (Table 4.4). Bay water salinity and pH were relatively consistent during the measurement campaigns. Therefore, it is evident that fluctuations in bay water temperature and equilibrium concentrations drive the direction of the ammonia flux in the Tampa Bay estuary, with elevated concentrations in the summer leading to ammonia emissions from the bay to the airshed. This is especially true at the Gandy Bridge site where it was discovered that air concentrations of ammonia are seasonally consistent, as discussed in Chapter 2. Summer bay water concentrations are elevated due to an increased direct and indirect wet deposition of ammonium from frequent thunderstorms (Chapter 3), and because ammonia equilibrium values are exponentially proportional to temperature, as benthic activity increases with water temperature in estuarine ecosystems (Larsen et al., 2001).

Previous unidirectional estimates of ammonia flux at the Gandy Bridge site were compared with current bi-directional flux calculations. Based on measurements made from 1996 through 2001, the average annual ammonia flux was calculated as 2.9 kg-NH\(_3\) ha\(^{-1}\) yr\(^{-1}\) (Poor, 2002). The improved summer flux (-117.9 µg-NH\(_3\) m\(^{-2}\) d\(^{-1}\)) was used to calculate the daily ammonia flux during the months of June, July, and August, and the annual ammonia flux was revised with these summer estimates. The adjusted average annual flux was then calculated as 2.0 kg-NH\(_3\) ha\(^{-1}\) yr\(^{-1}\), resulting in a 32% reduction in the estimated ammonia burden to Tampa Bay.
Several researchers suggest that air and water concentrations of ammonia decrease with distance from the shoreline and land-based sources (Asman et al., 1994; Barrett, 1998; Lee et al., 1998). This hypothesis is likely valid in the Tampa Bay estuary and therefore measurements made at a near-shore location may be overestimating ammonia flux rates. However, future studies involving the collection of more frequent offshore air and bay water ammonia and ammonium samples are necessary to substantiate this theory.

Modeled bi-directional ammonia flux rates were compared with gradient flux rates estimated for the Summer 2003 measurement campaign. Gradient fluxes were calculated as the product of the NOAA Buoy modeled deposition velocity, and the difference in concentration between the 6-m and 1-m annular denuders for each 24-hour measurement period. The modeled flux rates were calculated according to Equation 4.13, as previously mentioned. The modeled and gradient flux rates are not well correlated, as shown in Figure 4.20. The denuder measurements at 1 m above the MSL likely did not accurately represent the equilibrium concentrations of ammonia at the air/water interface. An attempt was made to locate the denuder assembly closer to the water surface. Due to tidal currents, however, there were several instances when bay water entered the denuder assembly each time, invalidating the sample. At a 1-m elevation, the denuder probably captured atmospheric ammonia that was transported to the site from ambient sources, due to the presence of a well-mixed atmospheric layer. The concentrations were likely influenced more by atmospheric concentrations than ammonia volatilization from the water surface, as is
evidenced by the large number of gradients within the 15% measurement error (Figure 4.20). Therefore, this method does not accurately predict ammonia flux rates over Tampa Bay and is not recommended as a viable sampling technique.

NOAA Buoy modeled ammonia flux estimates were also compared with Surface Renewal modeled flux estimates during Summer 2003 (Figure 4.21). The Surface Renewal model was developed to calculate the exchange rates of gases by simulating the continual turnover of air parcels at the air/water interface (see Schwarzenbach et al., 1993). The air/water transfer rates were calculated with the following equation:

\[ v_{d(gas)} = 0.2u_{10}\left[ \frac{D_{gas}}{D_{H2O}} \right]^{0.5} \]  

(Equation 4.20)

where \( u_{10} \) is the measured wind speed in m s\(^{-1} \) at 10 m above the water surface, 0.2\( u_{10} \) represents the air/water transfer rate of water vapor, \( D_{gas} \) is the gas phase molecular diffusion coefficient for ammonia at 298K (0.28 cm\(^2\) s\(^{-1}\)), and \( D_{H2O} \) is the molecular diffusion coefficient for water vapor at 298K (0.26 cm\(^2\) s\(^{-1}\)) (Incropera and DeWitt, 1985; Schwarzenbach et al., 1993). Equation 4.20 was deduced based on empirical correlations between wind speed, air/water transfer rates, and the molecular diffusivities of water vapor and the gas of interest.

The modeled ammonia flux rates were well correlated (Figure 4.21). A paired, two-tailed t-test indicated the modeled fluxes are not statistically different (\( p=0.96 \)) and a calculated \( R^2 \) value of 0.98 indicated that the Surface Renewal model is a practical alternative to the NOAA Buoy model, although the Surface Renewal model over predicts the fluxes relative to the NOAA Buoy model.
Figure 4.19 Net Exchange of NH₃ Between the Atmosphere and Tampa Bay for Three Measurement Periods. Positive Values Represent a Net Transfer of NH₃ from the Air to the Bay.

Figure 4.20 Comparison Between Modeled and Gradient Flux Estimates During Summer 2003. Stars Represent Atmospheric Gradients within the 15% Measurement Error.
Figure 4.21 Comparison Between NOAA Buoy Modeled and Surface Renewal Modeled Flux Estimates During Summer 2003

Table 4.3 Summary Statistics of NH$_3$ Flux Rates (µg-NH$_3$ m$^{-2}$ d$^{-1}$)

<table>
<thead>
<tr>
<th>Data</th>
<th>Mean</th>
<th>Median</th>
<th>Standard Deviation</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>November 2002</td>
<td>54.9</td>
<td>25.1</td>
<td>313.1</td>
<td>14</td>
</tr>
<tr>
<td>January 2003</td>
<td>137.4</td>
<td>166.7</td>
<td>157.6</td>
<td>14</td>
</tr>
<tr>
<td>Calibrated Summer 2003</td>
<td>-117.9</td>
<td>-62.4</td>
<td>743.2</td>
<td>29</td>
</tr>
</tbody>
</table>

Table 4.4 Average Air and Bay Water Equilibrium NH$_3$ Concentrations (µg m$^{-3}$)

<table>
<thead>
<tr>
<th>Data</th>
<th>$C_{air}$</th>
<th>$C_{eq}$</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>November 2002</td>
<td>0.84</td>
<td>0.41</td>
<td>14</td>
</tr>
<tr>
<td>January 2003</td>
<td>1.09</td>
<td>0.23</td>
<td>14</td>
</tr>
<tr>
<td>Summer 2003</td>
<td>1.93</td>
<td>2.76</td>
<td>29</td>
</tr>
</tbody>
</table>
4.7 Summary

Measured and modeled sensible heat flux (H) at the offshore Port Manatee Turn meteorological tower correlated well for the months of June through November 2002. Although the comparison was found to be statistically different ($p=3.8\times10^{-17}$), the average difference between the measured and modeled values was relatively small (Valigura, 1995). This supports Hypothesis 1 that the NOAA Buoy model is an effective tool for estimating the air/water exchange rates of ammonia over Tampa Bay when input parameters are measured offshore and over the water surface. A similar study was conducted to compare near-shore modeled results with offshore parameters to determine if the NOAA Buoy model accurately predicts over-water flux parameters when meteorological measurements are collected near-shore. The results indicate that differences between the near-shore and offshore modeled results were statistically different but relatively low during the fall season (Valigura, 1995), however, during the summer season, the model significantly under-predicts offshore flux parameters, supporting Hypothesis 2. These disparities are caused by the difference in land and water surface temperatures. The increased frequency of near-shore negative temperature differentials results in an underestimation of heat transfer between the water and air, which also results in a biased prediction of gas-phase mass transfer over coastal waters. The model was “calibrated” to more accurately predict over-water flux parameters during the summer season.
Daily, integrated bi-directional ammonia flux measurements were made for the summer, fall, and winter seasons at the Picnic Island Pier and Gandy Bridge research sites. Results indicate that during the fall and winter monitoring periods, the primary direction of the ammonia flux was from the air to the bay. However, during the summer monitoring period, there were several days when ammonia reemission from the bay to the airshed was calculated. This resulted in an overall negative emission rate and a 32% reduction in the estimated annual flux rate for ammonia. This study shows that volatilization of ammonia should be recognized as an important removal process from the Tampa Bay estuary. The results of this study support Hypothesis 3, providing evidence that ammonia flux rates are bi-directional, which reduces the ammonia burden available for biological synthesis in Tampa Bay.

The NOAA Buoy modeled flux rates were compared with gradient and Surface Renewal modeled flux rates during the summer season. It was determined that the gradient method does not accurately predict ammonia flux rates over Tampa Bay and is not recommended as a viable sampling technique. The NOAA Buoy modeled ammonia flux rates compared well with those calculated with the Surface Renewal model. The modeled results were not statistically different and highly correlated with an $R^2$ value of 0.98, indicating that the Surface Renewal model is a viable alternative for calculating the air/water exchange rates of ammonia over Tampa Bay.
CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

5.1 Conclusions

A greater understanding of the transport and deposition of ammonia to the Tampa Bay estuary is necessary as we progress toward the goal of maintaining bay nitrogen loadings and increasing seagrass coverage. This study investigated the local sources of ammonia in the Tampa Bay watershed, the effects of meteorological parameters on the transport of ammonia to the estuary, and the wet and dry processes controlling deposition of ammonia to Tampa Bay.

An ammonia emissions inventory was conducted for Pinellas, Hillsborough, and Polk counties, which are all located within the Tampa Bay watershed. The results of the inventory suggest that Polk County, located the furthest from the estuary to the east, contributed 55% of the emissions, with Hillsborough and Pinellas counties contributing 35% and 10%, respectively. The majority of Polk County’s emissions are from point, livestock, and fertilizer sources (84%). Hillsborough County’s emissions are dominated by livestock and fertilizer sources (62%). Pinellas County, one of the most densely populated and urbanized counties in the state of Florida, has dominant emissions from humans and domestic animals (58%). Hillsborough and Polk counties are both located to the east of Tampa Bay, while Pinellas County borders the western coastline of
the bay. Since a majority of the ammonia emitted in the region originates from Hillsborough and Polk counties (90%), a significant portion of the ammonia that is deposited to Tampa Bay is transported with continental air masses having an easterly flow.

Annual, seasonal, and diurnal ammonia and ammonium trends were explored at Gandy Bridge, an urban research site located along the eastern shoreline of Old Tampa Bay. A comparison of these trends was made with those discovered at Sydney, a rural research site located in eastern Hillsborough county. Annually, ammonia and ammonium concentrations were similar at both sites though seasonal variations differed between sites. Average concentrations at Gandy Bridge were seasonally consistent showing no considerable variation. Sydney, however, had significantly higher average ammonia concentrations during the spring and lower concentrations during the fall seasons. Diurnal variations at the sites were also inconsistent, with higher nighttime concentrations at Gandy Bridge and higher daytime concentrations at Sydney. A greater portion of ammonia is in the gas phase at the Sydney site, although at both sites, ammonia is in the gas phase the majority of the time. A statistical analysis of the datasets was conducted to determine if meteorological factors were responsible for these trends. It was determined that wind direction and air temperature were the most influential parameters affecting the Gandy Bridge and Sydney sites, respectively. These results show that concentrations at the Gandy Bridge site are consistent and likely affected by local transport from nearby industrial and agricultural sources located to the east of Tampa Bay, while the
rural Sydney site is likely affected by agricultural sources of ammonia that are temperature dependent. This suggests that controls on the large industrial and agricultural sources of ammonia in Hillsborough and Polk counties would significantly reduce the ammonia burden to the Tampa Bay estuary.

Sequential sampling of ammonium in wet deposition was conducted at the Gandy Bridge site to determine the intra-storm variability of this compound and the resulting effects on the Tampa Bay estuary. All of the monitored precipitation events were convective thunderstorms that formed over the Florida peninsula where numerous large fertilizer production facilities and agricultural properties are located. These storms then traveled west toward the Gulf of Mexico. During each precipitation event, the majority of ammonium was delivered to Tampa Bay at the initial stages of the storm. An aqueous phase accumulation model was used to predict sequential ammonium concentrations and results showed reasonable agreement between experimental and modeled values. A relationship between rainfall intensity and scavenging rate was also developed and will enable the calculation of this important input parameter in future studies that explore the relationship between the wet deposition of ammonium and ammonia reduction strategies. In fact, the ammonia scavenging coefficient algorithm developed during this study will replace the default values used in the ISC Short Term Wet Deposition model and the CALPUFF dispersion model for Tampa Bay.

The aqueous phase accumulation model was used to calculate ambient air ammonia concentrations prior to the start of each rainfall event, and these
values were compared with 24-hour averaged measured values at the Gandy Bridge site. Results showed that modeled values were between two and five times greater than measured values. These differences are likely due to the differing averaging periods between measured and modeled values and the in-cloud ammonium contribution.

The wet flux of ammonium was compared with atmospheric ammonia gradient measurements for the five events analyzed. The results of the analysis indicate that for four of the five events, a positive correlation exists between the wet flux of ammonium and ammonia emissions from the bay to the airshed, indicating that reemission of ammonia is possible following a rain event.

A comparison between AIRMoN samples collected concurrently with sequential samples was made to determine if diverse sampling techniques affect concentration results. On average, AIRMoN concentrations were between 50% and 95% of sequential concentrations for all five events. This trend suggests that chemical and/or biological transformations are occurring in the AIRMoN samples and that the sampling protocol produces results that underestimate wet deposition estimates of ammonium to the Tampa Bay estuary.

Measured and modeled offshore sensible heat flux (H) comparisons were useful in confirming the NOAA Buoy model as an effective tool for estimating the air/water exchange rates of ammonia over Tampa Bay. Near-shore and offshore modeled results were also compared and it was determined that the NOAA Buoy model adequately predicts flux parameters during the fall season, but under-predicts offshore flux parameters in the summer season. These disparities are
likely caused by the differences in land and water surface temperatures, with increased frequency of near-shore negative temperature differentials resulting in an underestimation of heat transfer between the water and air. The model was “calibrated” to more accurately predict over-water flux parameters during the summer season.

Daily, integrated bi-directional ammonia flux measurements were made for the summer, fall, and winter seasons at the Picnic Island Pier and Gandy Bridge research sites. Results indicate that during the fall and winter monitoring periods, the primary direction of the ammonia flux was from the air to the bay. However, during the summer monitoring period, there were several days when ammonia emissions from the bay to the air were calculated, resulting in a 32% reduction in the estimated annual flux rate of ammonia. This research shows that ammonia volatilization reduces the ammonia burden available for biological synthesis in Tampa Bay and should be recognized as an important removal process from the estuary.

The NOAA Buoy modeled flux rates were compared with gradient and Surface Renewal modeled flux rates during the summer season. It was determined that the gradient method does not accurately predict ammonia flux rates over Tampa Bay and is not recommended as a viable sampling technique. The NOAA Buoy modeled ammonia flux rates compared well with those calculated with the Surface Renewal model. The modeled results were not statistically different and highly correlated with an $R^2$ value of 0.98, indicating that
the Surface Renewal model is a viable alternative for calculating the air/water exchange rates of ammonia over Tampa Bay.

This study has revealed that ammonia flux rates in Tampa Bay are comparable with those calculated for the North Sea, but lower than those found in the Chesapeake Bay estuary. Ammonia is deposited to the Tampa Bay estuary via wet and dry deposition when winds follow an easterly trajectory. Therefore, the magnitude of local ammonia sources in the eastern section of the Tampa Bay watershed suggests that emission reductions could significantly reduce atmospheric ammonia deposition into Tampa Bay. Smith (2003) suggests several ammonia reduction strategies. The most efficient method would involve controlling fugitive emissions from fertilizer production facilities that are located along the eastern edge of Hillsborough Bay in the Port of Tampa. Significant reductions in agricultural emissions can also be obtained using soil injection of fertilizers and covered animal waste lagoons to reduce ammonia volatilization from these sources.

5.2 Recommendations for Future Research

This study revealed that 90% of the local ammonia emissions are produced by sources located east of Tampa Bay, in Hillsborough and Polk counties. It is recommended that dispersion modeling be conducted on ammonia sources located in these counties to determine the emission control strategies that would most effectively reduce ammonia transport and deposition to the Tampa Bay estuary.
The wet deposition process contributes a considerable quantity of ammonium to the Tampa Bay estuary. This study discovered that during convective thunderstorms in the summer season, a majority of the ammonium is deposited during the initial stages of the storm. In addition, a relationship between precipitation intensity and scavenging rate enables the prediction of rainfall concentrations of ammonium during these types of storm events. Future research on frontal storms that typically occur during the fall, winter, and spring seasons is necessary to determine if ammonium concentrations also follow a power regression relationship for this category of storms, and if this trend can also be accurately modeled. Additional research on the relationship between wet deposition of ammonium and ammonia volatilization from the bay is necessary to determine if this phenomenon is seasonally variable and if boundary conditions can be ascertained.

Several researchers suggest that air and water concentrations of ammonia decrease with distance from the shoreline and land-based sources. Currently, it is necessary that ammonia flux sampling is made near-shore due to power and accessibility constraints. As technology becomes more sophisticated and instrumentation more refined, it is recommended that future studies involving the collection of simultaneous offshore air and bay water ammonia and ammonium measurements occur at a greater spatial resolution to determine offshore ammonia flux rates to Tampa Bay with increased accuracy.
Additional research is also necessary to determine if the ammonia that is volatilized from Tampa Bay is conserved within the atmospheric mixed layer and re-deposited to the estuary, as several authors suggest.

Finally, the AIRMoN sampling protocol underestimates wet deposition estimates of ammonium to the Tampa Bay estuary. Further investigation into this finding is necessary to determine if chemical and/or biological transformations of ammonium are occurring in the AIRMoN samples. It is suggested that if future research substantiates this theory, recommendations be made to the program managers to remedy the loss of ammonium in precipitation, so that accurate ammonium wet deposition estimates are made for Tampa Bay.
REFERENCES


189


Mizak, C. A. (2001). *Tampa Bay Ammonia Emissions Inventory*. Atmospheric Deposition Research and Monitoring in Tampa Bay: The First Five Years and the Next Five Years, University of South Florida, Tampa, FL.


Appendix A: Results of Regression Modeling at Gandy Bridge and Sydney

Multiple Linear Regression – Gandy Bridge

SYSTAT Rectangular file C:\Program Files\SYSTAT 10.2\gandy12hour.SYD, created Tue Nov 25, 2003 at 09:33:34, contains variables:

<table>
<thead>
<tr>
<th></th>
<th>LNNH3</th>
<th>TEMP</th>
<th>RH</th>
<th>WS</th>
<th>SINWD</th>
<th>COSWD</th>
</tr>
</thead>
</table>

Dep Var: LNNH3  N: 62  Multiple R: 0.432  Squared multiple R: 0.187
Adjusted squared multiple R: 0.173  Standard error of estimate: 0.756

<table>
<thead>
<tr>
<th>Effect</th>
<th>Coefficient</th>
<th>Std Error</th>
<th>Std Coef</th>
<th>Tolerance</th>
<th>t</th>
<th>P(2 Tail)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONSTANT</td>
<td>0.211</td>
<td>0.107</td>
<td>0.000</td>
<td>.</td>
<td>1.967</td>
<td>0.054</td>
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<tr>
<td>SINWD</td>
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<td>0.432</td>
<td>1.000</td>
<td>3.713</td>
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Analysis of Variance

<table>
<thead>
<tr>
<th>Source</th>
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<th>df</th>
<th>Mean-Square</th>
<th>F-ratio</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
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<td>7.876</td>
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<tr>
<td>Residual</td>
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<td></td>
</tr>
</tbody>
</table>

Durbin-Watson D Statistic 1.045
First Order Autocorrelation 0.431
Appendix A: (Continued)

Dep Var: LNNH3  N: 62   Multiple R: 0.541   Squared multiple R: 0.293
Adjusted squared multiple R: 0.269   Standard error of estimate: 0.711

<table>
<thead>
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<th>Std Coef</th>
<th>Tolerance</th>
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<th>P(2 Tail)</th>
</tr>
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<td>TEMPHUM</td>
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Analysis of Variance

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<th>Mean-Square</th>
<th>F-ratio</th>
<th>P</th>
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<td>Resid</td>
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<td></td>
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</table>

Durbin-Watson D Statistic 1.266
First Order Autocorrelation 0.321
Appendix A: (Continued)

Multiple Linear Regression

SYSTAT Rectangular file C:\Program Files\SYSTAT 10.2\Sydney12hour.syd, created Mon Nov 24, 2003 at 13:01:12, contains variables:

| Variable | LNNH3 | TEMP | RH | WS | WD |

Dep Var: LNNH3  N: 49  Multiple R: 0.537  Squared multiple R: 0.288

Adjusted squared multiple R: 0.273  Standard error of estimate: 0.438

<table>
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<tr>
<th>Effect</th>
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<th>Std Coef</th>
<th>Tolerance</th>
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<th>P(2 Tail)</th>
</tr>
</thead>
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</table>

Analysis of Variance

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<th>Source</th>
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<th>Mean-Square</th>
<th>F-ratio</th>
<th>P</th>
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</thead>
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<tr>
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<td>Residual</td>
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Durbin-Watson D Statistic 1.544
First Order Autocorrelation 0.222
Appendix B: Results of Principle Components Analysis at Gandy Bridge and Sydney

Principle Components Analysis – Gandy Bridge
Matrix to be factored

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<tr>
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<th>LNNH3</th>
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<th>RH</th>
<th>WS</th>
<th>SINWD</th>
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<tr>
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<tr>
<td>TEMP</td>
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<td>1.000</td>
<td>-0.567</td>
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<tr>
<td>RH</td>
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<td>COSWD</td>
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</table>

Latent Roots (Eigenvalues)

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<tr>
<th></th>
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<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.445</td>
<td>1.557</td>
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<td>6</td>
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</table>

Empirical upper bound for the first Eigenvalue = 2.9878.

Chi-Square Test that all Eigenvalues are Equal, N = 62
CSQ = 144.9512  P = 0.0000  df = 15.00

Chi-Square Test that the Last 3 Eigenvalues Are Equal
CSQ = 12.1454  P = 0.0498  df = 5.70
Appendix B: (Continued)

Latent Vectors (Eigenvectors)

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>WS</td>
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<tr>
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<tr>
<td>RH</td>
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<tr>
<td>LNNH3</td>
<td>0.201</td>
<td>-0.020</td>
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Standard Error for Each Eigenvector Element

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<tr>
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<th>3</th>
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</thead>
<tbody>
<tr>
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<tr>
<td>SINWD</td>
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<td>0.107</td>
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<td>RH</td>
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Component loadings

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Variance Explained by Components

<table>
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<tr>
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<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.445</td>
<td>1.557</td>
<td>1.120</td>
</tr>
</tbody>
</table>
Appendix B: (Continued)

Percent of Total Variance Explained

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
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</thead>
<tbody>
<tr>
<td>40.754</td>
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Rotated Loading Matrix (VARIMAX, Gamma = 1.0000)

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<tr>
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<th>3</th>
</tr>
</thead>
<tbody>
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</tr>
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<td>0.029</td>
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"Variance" Explained by Rotated Components

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<tr>
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</tr>
</thead>
<tbody>
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<td>1.251</td>
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Percent of Total Variance Explained

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<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>37.814</td>
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</table>

Differences: Original Minus Fitted Correlations or Covariances

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<tr>
<th>COSWD</th>
<th>WS</th>
<th>SINWD</th>
<th>TEMP</th>
<th>RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>COSWD</td>
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<td></td>
</tr>
<tr>
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</table>

LNNH3 | 0.063 |
Appendix B: (Continued)

Principle Components Analysis – Sydney
Matrix to be factored

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<thead>
<tr>
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<th>LNNH3</th>
<th>TEMP</th>
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<th>WS</th>
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Latent Roots (Eigenvalues)

<table>
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<th>4</th>
<th>5</th>
</tr>
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</table>

Empirical upper bound for the first Eigenvalue = 2.9798.

Chi-Square Test that all Eigenvalues are Equal, N = 49
CSQ = 101.4180  P = 0.0000  df = 10.00

Chi-Square Test that the Last 3 Eigenvalues Are Equal
CSQ = 19.5893  P = 0.0029  df = 5.83
Appendix B: (Continued)

<table>
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<tr>
<th></th>
<th>Component 1</th>
<th>Component 2</th>
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<tbody>
<tr>
<td>RH</td>
<td>-0.585</td>
<td>0.017</td>
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<tr>
<td>WS</td>
<td>0.461</td>
<td>-0.427</td>
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<tr>
<td>LNNH3</td>
<td>0.456</td>
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</tr>
<tr>
<td>TEMP</td>
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<td>0.507</td>
</tr>
<tr>
<td>WD</td>
<td>-0.181</td>
<td>0.712</td>
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Standard Error for Each Eigenvector Element

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<tr>
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<tbody>
<tr>
<td>RH</td>
<td>0.045</td>
<td>0.179</td>
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<tr>
<td>WS</td>
<td>0.131</td>
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<td>LNNH3</td>
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<td>0.148</td>
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<tr>
<td>WD</td>
<td>0.206</td>
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Component loadings

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<tr>
<td>RH</td>
<td>-0.912</td>
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<td>0.719</td>
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<td>LNNH3</td>
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Variance Explained by Components

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<tr>
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<td>2.431</td>
<td>1.474</td>
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Percent of Total Variance Explained

<table>
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<th>Component 2</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>48.628</td>
<td>29.471</td>
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Appendix B: (Continued)

Rotated Loading Matrix (VARIMAX, Gamma = 1.0000)

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<tr>
<td>TEMP</td>
<td>0.916</td>
<td>0.188</td>
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<td>RH</td>
<td>-0.783</td>
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<td>LNNH3</td>
<td>0.759</td>
<td>-0.103</td>
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<tr>
<td>WD</td>
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<td>0.891</td>
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<tr>
<td>WS</td>
<td>0.371</td>
<td>-0.805</td>
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</table>

"Variance" Explained by Rotated Components

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</thead>
<tbody>
<tr>
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<td>2.199</td>
<td>1.706</td>
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</tbody>
</table>

Percent of Total Variance Explained

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<tbody>
<tr>
<td></td>
<td>43.984</td>
<td>34.116</td>
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</table>

Differences: Original Minus Fitted Correlations or Covariances

<table>
<thead>
<tr>
<th></th>
<th>TEMP</th>
<th>RH</th>
<th>LNNH3</th>
<th>WD</th>
<th>WS</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEMP</td>
<td>0.125</td>
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<td></td>
<td></td>
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<tr>
<td>RH</td>
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<td>0.168</td>
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<tr>
<td>LNNH3</td>
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<td>0.413</td>
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</tr>
<tr>
<td>WD</td>
<td>-0.058</td>
<td>-0.033</td>
<td>-0.089</td>
<td>0.174</td>
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<tr>
<td>WS</td>
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<td>0.035</td>
<td>-0.080</td>
<td>0.171</td>
<td>0.214</td>
</tr>
</tbody>
</table>
ABOUT THE AUTHOR

Constance Anne Mizak received her B.S. in Industrial Engineering in 1994 and M.S. in Environmental Engineering in 1996 from the New Jersey Institute of Technology, in Newark, NJ. During her doctoral studies at USF, she received a National Water Research Institute fellowship to study environmental policy at the U.S. Department of the Interior and the Environmental Protection Agency in Washington, D.C. She has published and presented the results of her research at four national and regional meetings of the Air and Waste Management Association. She also received two awards for her research studies.

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