

Report for 2002FL5B: The Flux of Ammonia at the Air/Water Interface of Tampa Bay

- Conference Proceedings:
 - Mizak, C.A., Poor, N.D., 2002. Ammonia Flux at the Air/Water Interface of Tampa Bay. Proceedings of the 95th Annual Air & Waste Management Conference and Exhibition, June 23-27, Baltimore, MD, A&WMA, Pittsburgh, PA.
- Other Publications:
 - Mizak, C.A., Poor, N.D., 2002. Ammonia Flux at the Air/Water Interface of Tampa Bay. The Florida Air & Waste Management Association Annual Meeting, September 15-17, Jupiter, FL.
 - USF Health Science Center Research Day on February 13, 2003 and awarded a prize for superior presentation:
<http://www.hsc.usf.edu/PUBHEALTH/GRANTS/HSCResearchDay2003.html>

Report Follows:

Title: The Flux of Ammonia at the Air/Water Interface of Tampa Bay

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Problem and Research Objectives:

Tampa Bay is one of the largest and most diverse estuaries on the West Coast of Florida and contributes over \$5-billion annually to the region from trade, tourism, development and fishing. Over the past fifty years, unchecked pollution destroyed more than half of the bay's sea grass meadows and contributed to a decline in the number of important species native to the region. Since the Tampa Bay Estuary Program (TBEP) was established in 1991, several key action initiatives were defined to improve conditions in the bay and return it to a viable state. Atmospheric deposition of nitrogen was identified as a key action initiative in the program because it is expected to increase with population, power consumption, and traffic growth. To better quantify nitrogen deposition to the bay, the Florida Department of Environmental Protection, in conjunction with the TBEP, developed the BRACE (Bay Regional Atmospheric Chemistry Experiment) program. The goals of BRACE are to estimate the direct deposition of biologically active nitrogen to Tampa Bay, to apportion the regional source contributions to this deposition, and to assess Tampa Bay's air quality before and after the Gannon station re-powering. Understanding the mechanisms that contribute to atmospheric ammonia deposition to the bay is an important component of this study.

Recent nitrogen deposition research in the estuary indicates that ammonia deposition dominates the total dry nitrogen flux to the bay. Gaseous plus aerosol ammonia contribute approximately 450 tons per year or 60% of the total nitrogen deposition of 760 tons per year to the estuary. Research data also indicate that during the summer months, Tampa Bay may act as a source for atmospheric ammonia as the water temperature increases and ammonium concentrations become elevated. To better quantify the contribution of ammonia to the annual inputs of new nitrogen, the daily flux of ammonia will be calculated at the air/water interface to quantify the seasonal and temporal patterns of atmospheric ammonia deposition to Tampa Bay.

Objectives:

1. Describe the direction and magnitude of the ammonia flux at the air/water interface;
2. Determine if estuarine meteorological conditions and bay salinity cause a bi-directional ammonia flux;

3. Accurately estimate the temporal patterns of atmospheric ammonia deposition;
4. Utilize analysis of ambient measurement data to test and improve algorithms that calculate the flux of ammonia at the air/water interface; and
1. Explore the variation between measured data and modeled fluxes to reduce or explain any observed error.

Methodology:

Flux measurements were derived from one year of seasonal integrated daily monitoring data collected over Tampa Bay. Intensive data collection occurred daily over three, 2-week sampling periods to discern the effects of temporal variability on the dry deposition of ammonia to the bay. The Gandy Bridge monitoring site was utilized for the April 2002 sampling and the Picnic Island Pier site was utilized during the November 2002 and January 2003 sampling events. Gaseous and aerosol ammonia were collected using a URG Inc. annular denuder system (ADS). The ADS operated at an airflow of 10 L/min for 12 hours and consisted of a 2.5 μ m particle cutpoint cyclone inlet, 150 mm gas denuder and a filter pack containing a 47 mm diameter/1 μ m pore size nylon filter. The denuders and filters were extracted with DI water and analyzed for ammonia with an ion chromatograph (IC). Water grab samples were analyzed in the laboratory by automated colorimetry for ammonium concentrations. The net ammonia flux was calculated as the product of the difference of the average daily and equilibrium ammonia air concentrations and the average daily deposition velocity. The ammonia equilibrium concentration was calculated based on Henry's Law through measurements of bay salinity, temperature, pH and ammonium concentrations. The NOAA inferential buoy model was used to calculate the average daily gaseous and aerosol ammonia deposition velocities.

Measurements taken during each sampling event included:

- ◆ Hourly wind speed and direction – NOAA CO-OPS (8726607 Old Port Tampa, FL)
- ◆ Hourly air temperature and relative humidity – Omega RHTEMP 1000 probe
- ◆ Hourly bay water temperature, pH, and salinity – HYDROLAB minisonde
- ◆ Diurnal collection of bay water samples – analyzed for NH₃-N by automated colorimetry
- ◆ Diurnal NH_x measurements – URG Annular Denuder System

Principal Findings and Significance:

- ◆ *Describe the direction and magnitude of the ammonia flux at the air/water interface;*

Ammonia flux calculations were made using ambient monitoring data that included atmospheric and bay water ammonia and ammonium concentrations and meteorological measurements. The measurements were used as inputs to the NOAA Buoy model to calculate the deposition velocities of gaseous ammonia. Monitoring and subsequent flux

calculations occurred over three sampling periods: April 2002, November 2002, and January 2003. During April 2002, the 24-hour average flux was 2.57 g/ha and the daily and nightly average fluxes were 1.35 and 3.79 g/ha, respectively. The November 2002 24-hour, daily, and nightly average fluxes were 0.72, 0.68, and 0.75 g/ha, respectively. The January 2003 24-hour, daily, and nightly average fluxes were 0.62, 0.52, and 0.70 g/ha, respectively. It is important to note that the April 2002 average fluxes were considerably greater than the fall and winter average flux calculations. It is likely that this seasonal trend is due to the dependence of ammonia emission strength on local climate. Based on U.S. EPA data, it is estimated that the agricultural sector contributes approximately 85% of U.S. ammonia emissions. An ammonia emission inventory completed for Hillsborough County, Florida indicated that approximately 62% of county ammonia emissions originated from livestock and fertilizer applications, with only approximately 8% from point sources. Since the majority of emissions originate from agricultural sources, it is possible that the higher average temperature and relative humidity in the spring season would cause greater volatilization of ammonia from the land. Because ammonia has a short residence time in the atmosphere and is highly soluble in water, the increased volatilization and ambient concentrations would contribute to an increase in ammonia flux to Tampa Bay.

During the three monitoring periods, the direction of ammonia flux was from the air to the water, with few exceptions. The direction of flux is dependent on the ambient air concentrations of gaseous ammonia, bay water concentrations of ammonium, and the Henry's Law equilibrium theory. The majority of the time, the atmospheric ammonia concentrations are high enough that the ammonia flux is positive and ammonia is deposited to the bay. However, when bay water concentrations become elevated, the ammonium ion dissociates to ammonia gas and hydrogen ion, which drives the flux from the water to the air. There were several times during the sampling when this occurred.

◆ *Determine if estuarine meteorological conditions cause a bi-directional ammonia flux;*

During the November 2002 and January 2003 sampling events, there were three times when a large negative flux (from water to air) was calculated. The negative fluxes were due to a simultaneous decrease in measured ambient concentrations and an increase in bay water concentrations of ammonia. Upon further analysis, it was discovered that these events followed significant rainstorms that contributed greater than 0.2 inches of precipitation. Our hypothesis is that the precipitation directly and indirectly transferred ammonia to the bay and substantially increased the bay water concentration of ammonium while decreasing the ambient air concentrations of ammonia. This in turn triggered an ammonia flux from the bay back to the airshed.

◆ *Accurately estimate the temporal patterns of atmospheric ammonia deposition;*

The two air monitoring sites, Gandy Bridge and Picnic Island Pier, are located adjacent to Tampa Bay along the western edge of Hillsborough County. The majority of local ammonia sources, including the agricultural and industrial sources, are located in eastern Hillsborough County. Therefore, one would expect to find increased ammonia fluxes

when the winds were coming from the east/southeast direction. Comparing daily and nightly fluxes with wind speed and direction for the three monitoring periods, reasonable correlations were discovered. During the April 2002 period, daily fluxes increased for winds between 7 and 9 m/s and 120 to 180 degrees (SE of the monitoring site). Nightly fluxes were greater than daytime fluxes and increased substantially with winds between 6 and 7 m/s and 100 to 180 degrees (E/SE of the site). Although the November 2002 and January 2003 monitoring periods did not show strong correlations with wind direction, wind speed correlations did remain strong with increased fluxes occurring at moderate wind speeds for both daily and nightly comparisons. In general, increases in ammonia flux only occurred with wind speeds less than 6 m/s. One reason for the absence of a wind direction correlation during these periods may be the low ambient concentrations of gaseous ammonia during the fall and winter seasons. The decrease in ammonia volatilization from agricultural sources at cooler temperatures coupled with a strong thermal buoyancy is most likely causing increased mixing at higher atmospheric elevations, thereby diluting the already low ambient ammonia concentrations. However, the consistent trend with moderate wind speeds can be explained by the short atmospheric residence time for ammonia. Local source emissions are remaining in the area under these wind speed conditions.

- ◆ *Utilize analysis of ambient measurement data to test and improve algorithms that calculate the flux of ammonia at the air/water interface; and*
- ◆ *Explore the variation between measured data and modeled fluxes to reduce or explain any observed error;*

The NOAA Buoy model was utilized to estimate the air/water exchange rates of ammonia over Tampa Bay. In the model, the standard bulk transfer coefficient equations for mass, heat, and momentum were used to derive expressions for temperature and wind speed gradients. The model was developed to use over-water meteorological parameters as inputs, which include wind speed, air and water temperature, and relative humidity. Iteration was performed until measured temperature and wind speed gradients equaled the calculated values. Model outputs include gas and particle deposition velocity, sensible and latent heat flux, and friction velocity.

The NOAA Buoy model was tested with data recorded at an offshore meteorological tower. Meteorological and bay water measurements recorded at the Port Manatee Turn meteorological tower, which is located in the middle of Tampa Bay, were used as inputs to the model, and the model outputs were compared with direct measurements of sensible heat flux and friction velocity taken at the tower. Differences between the modeled and the measured sensible heat flux and friction velocity were less than 4% and 2%, respectively, indicating that the model accurately predicts these parameters when measurements are recorded offshore.

A study was then conducted to determine if turbulent flux parameters are accurately predicted with near-shore measurements as inputs to the NOAA Buoy model. Meteorological and bay water measurements recorded at the Picnic Island Pier over the same time period were then used as inputs to the NOAA Buoy model, and the model

outputs were also compared with the direct measurements of sensible heat flux and friction velocity taken at the tower.

Although a consistent trend between modeled and measured sensible heat flux and friction velocity can be seen over the 2-week period, the modeled results are consistently lower than the measured parameters. For the November 2002 data, on average, the modeled and measured sensible heat fluxes were 23.3 W/m² and 39.2 W/m², respectively, indicating that over this time period the model underestimated the sensible heat flux by approximately 40%. Likewise, the average modeled and measured friction velocities were 0.18 m/s and 0.24 m/s, respectively, indicating the model underestimated the friction velocity by approximately 25%.

During January 2003, average modeled and measured sensible heat fluxes were 15.1 W/m² and 22.2 W/m², respectively, indicating that the model underestimated the sensible heat flux by approximately 32%. The average modeled and measured friction velocities were 0.13 m/s and 0.17 m/s, respectively, again indicating the model underestimated the friction velocity by approximately 24%.

It is apparent that there is a consistent trend with the NOAA Buoy model underestimating direct over water measurements of sensible heat flux and friction velocity when meteorological input parameters are recorded near-shore. This may be due to the fact that the model was developed with meteorological parameters recorded from a buoy located offshore in coastal waters. For this study, the meteorological measurements were taken at sites located adjacent to Tampa Bay. The effects of land elements on wind speed and air and water temperatures may have skewed the model results causing an underestimation of the flux parameters. Based on the results of this study, the NOAA Buoy model, when using input data recorded near land, may be underestimating the deposition velocity by between 30 and 40%.