Contribution of Industrial Atmospheric Ammonia Emissions to Nitrogen Loading in the Tampa Bay Estuary, Tampa, FL, USA

Noreen Poor
University of South Florida College of Public Health, 13201 Bruce B. Downs Blvd., Tampa, FL 33612; 813.974.8144; 813.974.4986 FAX; npoor@hsc.usf.edu.

Abstract

We used the CALMET/CALPUFF modeling system to simulate for May 2002 the emission, dispersion, and transport of ammonia (NH_3) released from the fertilizer industry in west central Florida, based on SIC codes and annual emission rates reported in the 2001 USEPA toxic release inventory. For May 2002 at the Gandy Bridge monitoring site, which is adjacent to Tampa Bay, the modeled and measured 12-hour average ammonia plus ammonium (NH_y) concentrations were 0.5 μg m^{-3} and 2.5 μg m^{-3}, respectively. We estimated that the direct dry deposition of atmospheric NH_3 from the fertilizer industry was 0.06 kg-N ha^{-1} mo^{-1} (6 metric tons), compared with 0.34 kg-N ha^{-1} mo^{-1} (35 metric tons) from all sources. This loading rate represented ~10% of the total direct deposition (wet + dry) of nitrogen to Tampa Bay.

1. Introduction

Central Florida has one of the world's richest reserves of phosphate ore, which is mined and processed locally into ammonium phosphate fertilizers. Associated activities that release ammonia (NH_3) to the atmosphere include the off-load of NH_3 from ship to shore, transport of NH_3 via pipeline from port to plant, and the manufacture, storage and transport of ammonium phosphate products. Fertilizer industry in two counties accounted for ~80% of the NH_3 emissions reported in the USEPA Toxic Release Inventory (USEPA, 2004) for a 3-county area surrounding Tampa Bay, but only ~10% of the total NH_3 emissions for these three counties when non-point sources are included (Mizak, 2004). Refer to Table 1 for a summary of the NH_3 emissions for the fertilizer industry.

Poor, et al. (2001) estimated that the direct dry deposition of atmospheric NH_3 contributed 2.30 kg-N ha^{-1} yr^{-1} (240 metric tons) to Tampa Bay, or ~30% of the total direct atmospheric nitrogen deposition. To assess the contribution of the fertilizer industry on nitrogen loading to Tampa Bay, we ran the CALMET/CALPUFF model to simulate for May 2002 the emission, dispersion, and transport of ammonia (NH_3) released from fertilizer industries in Hillsborough and Polk Counties, Florida. The direct dry deposition flux was calculated from the NH_3 concentrations predicted for the Gandy Bridge monitoring site (27.89 ^{o}N, 82.54 ^{o}W), using an approach consistent with that described by Poor, et al. (2001).

Table 1
Ammonia emissions from fertilizer industries near Tampa Bay (TRI, 2004).

Facility	County	Latitude (°N)	Longitude (°W)	2001 Total Air Emissions (Mt yr^{-1})	Map ID
Cargill Fertilizer Inc.	Polk	27.9066	81.9186	34	6
Cargill Fertilizer, Inc.	Hillsborough	27.8623	82.393	539	8
CF Industries, Inc.	Hillsborough	28.1662	82.1401	23	10
CF Industries, Inc.	Polk	27.8647	81.9317	319	4
Farmland Hydro LP	Hillsborough	27.9063	82.417	17	7
Farmland Hydro LP	Polk	27.8431	81.8613	368	2
Nitram, Inc.	Hillsborough	27.9101	82.3949	164	3
Trademark Nitrogen Corp.	Hillsborough	27.9547	82.3532	2	9
US Agri-Chemicals Corp	Polk	27.9017	81.8804	47	5
US Agri-Chemicals Corp	Polk	27.7426	81.8512	56	1

2. Materials and Methods

The CALMET/CALPUFF model has three components: CALMET, a meteorological model with a diagnostic wind field generator; CALPUFF, a dispersion model; and CALPOST, a post-processing program for the calculation of time-averaged concentrations and deposition fluxes from the CALPUFF output. Default model control parameters for the modeling system were used as much as possible.

To help analyze data acquired in May 2002 for the Bay Regional Atmospheric Chemistry Experiment, SSESCO, Inc. (St. Paul, MN) produced CALMET model (Version 5.22, Level 020828) input files for a 600 x 900 km modeling domain over peninsular Florida on a 10-km grid scale with 12 vertical layers. They began with the three dimensional meteorological fields from an archived NOAA North American Rapid Update Cycle (RUC2) prognostic model, which assimilates surface and upper air observations, satellite and radar data into a weather forecast. The RUC2 model was run with a one-hour resolution for 40 km grid cells and 40 vertical layers and was used as a first guess for a mesoscale data assimilation using the Advanced Regional Prediction System (ARPS) Data Assimilation System (ADAS) and metar observations. The resulting mesoscale temperature, pressure, wind, and humidity fields were checked by SSESCO with an objective data analysis technique and used in CALMET as a first guess wind field and as virtual surface and upper air observations spaced across the modeling domain for the CALMET objective analysis procedure. The CALMET model provides as output hourly winds and temperatures for a three dimensional modeling domain, and hourly two-dimensional outputs of mixing heights and surface characteristics (Scire, et al., 2000). We recompiled the CALMET input files for a 210 km x 210 km modeling domain over central Florida on a 1.5 km grid scale with 12 vertical layers.

We ran the three-dimensional, non-steady state, Lagrangian CALPUFF model (Version 5.511, Level 020828) to simulate the emission, dispersion, and transport NH_3 released from the fertilizer industry. Calculation of the time-dependent transformation of NH_3 to NH_4 was not a feature of the CALPUFF model. Inputs required by CALPUFF for NH_3 modeling were the three-dimensional meteorological fields produced by CALMET, emission source data and receptor grid configuration. Dry and wet deposition of NH_3 to the surface was not modeled, representing a positive bias in the results.

The emissions data were obtained from the USEPA Toxic Release Inventory (USEPA, 2004), and included both fugitive and stack air emissions. For each of the 10 sources (Table 1), we verified from 1998-1999 aerial photographs (Terraserver, 2004) that the geographical coordinates matched the location of the industrial facility, and used to photographs to get an approximate release area for the fugitive emissions. The release area represented the industrial operations not including the waste processing ponds or gypsum stacks. Information on the stack parameters, e.g., stack height, diameter, exit velocity, and temperature, were gleaned from the USEPA 1999 NET database (USEPA, 2003). If the stack parameters were not explicitly given for NH_3 emissions, we used the stack parameters for collocated SO_2 emissions. Stack emissions were aggregated into a single stack for facilities with multiple stacks. Typically, the reported stack parameters for multiple stacks were identical. Reported emissions were in lbs yr^{-1} and were converted to g s^{-1} for input to the CALPUFF model. Inherent in this assumption is that the stacks operated at a constant emission rate for 8,760 hrs yr^{-1}. The effect of this assumption is a negative bias in the results.

The CALMET/CALPUFF modeling system was run for May 2002, and the output hourly concentrations at the geographical coordinates for the Gandy Bridge site were averaged from 0700 EST to 1900 EST and 1900 EST to 0700 EST for comparison with integrated measurements of NH_3 (and NH_4) available at this location (Mizak, 2004).

Deposition velocities were calculated with the University of South Florida website (Version1) of the integrated NOAA buoy model/Williams model (Bhethanabotla, 2004), The NOAA buoy model is an iterative bulk exchange model developed for highly water-soluble gases and requires as inputs air temperature, water temperature, wind speed and relative humidity. Six-minute averaged measurements of air temperature; water temperature, 10-m wind speed, and 10-m relative humidity were obtained from a monitoring station located in Tampa Bay ~25 km south southwest of the Gandy Bridge air monitoring site. This site began operation on May 6, 2002.

Deposition velocities were calculated for every six minutes of meteorological data and averaged over 12 hours. Deposition rates were calculated from 12-hour averages of concentrations and deposition velocities. For those five days in early May for which mid-bay meteorological data were not available, we substituted average daytime and

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nighttime deposition velocities into the flux calculations. The dry deposition rate of NH_y-N (F_N) was calculated as the product of the ambient air concentration (C_N) and deposition velocity (v_d), with units of μg-N m^{-2} s^{-1}, μg-N m^{-3}, and m s^{-1}, respectively (Equation 1).

Equation 1. $F_N = C_N \cdot v_d$

The NH_y-N flux computed in this manner assumes that NH_3 evasion from the water need not be considered, that the deposition velocity and NH_3 concentrations are not covariant, and that the NH_y-N flux $\cong$ NH_3-N flux. A bi-directional flux at the air/water interface in the absence of heavy rainfall can lower NH_3-N deposition by 10% to 20% (Mizak, 2004; Poor, et al., 2001); thus, this assumption yields a positive bias. The NOAA buoy model predicts (somewhat) higher deposition velocities at nighttime when the NH_3 concentrations are higher, thus this assumption gives our results a negative bias. Finally, deposition velocities for fine particulate NH_4 are a factor of 10 or lower than those for NH_3, so this last assumption is reasonable. The average ratio of measured NH_3 to NH_y was 71% and we multiplied the modeled (untransformed) NH_3 concentrations by this ratio to get a more realistic average NH_3 concentration before calculating a deposition rate.

3.0 Results and Discussion

The modeled NH_3 concentrations shown in Fig. 1 and Fig. 2 clearly indicate a contribution from the fertilizer industry, and explained 38% of the variability in the measured NH_3 concentrations. Some portion of the NH_3 will convert to NH_4 during the transport time from the emission point to the monitoring site, however, the extent of this conversion was not predicted by the CALPUFF model. The residence time of NH_3 in the atmosphere extends up to ~10 d (Seinfeld and Pandis, 1998), and it is typically removed through wet and dry deposition and by reacting with H_2SO_4 to form ammonium bisulfate or ammonium bisulfate. While the correlation of modeled with measured NH_3 concentrations at the Gandy Bridge site is statistically significant, no correlation was apparent between the modeled NH_3 concentrations and measured NH_4 concentrations.

The modeled and measured average NH_y concentrations at the Gandy Bridge site were 0.5 μg m^{-3} and 2.5 μg m^{-3}. Nighttime concentrations were higher than daytime for both measured and modeled NH_y concentrations: 2.0 μg m^{-3} and 0.2 μg m^{-3} for the respective daytime concentrations and 3.0 μg m^{-3} and 0.7 μg m^{-3} for the respective nighttime concentrations. This trend can be explained by the presence of a land-sea breeze on many hot days that carried the NH_3 plumes inland during the day, and by the combination of a stable atmospheric and flow of air from east to west that kept the plumes reasonably intact (Fig. 2) during the night.

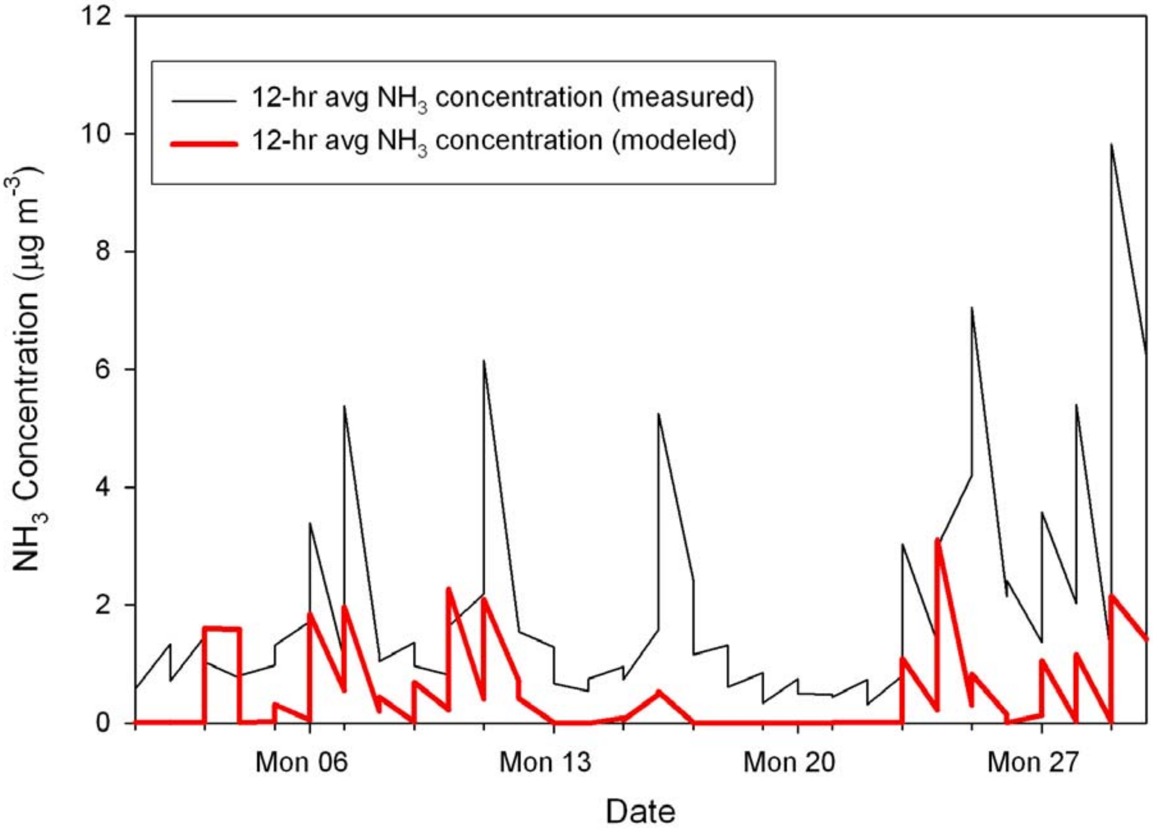

Fig. 1. 12-hr average NH_3 modeled and measured concentrations at the Gandy Bridge site. Modeled concentrations represent the contribution from the fertilizer industry.

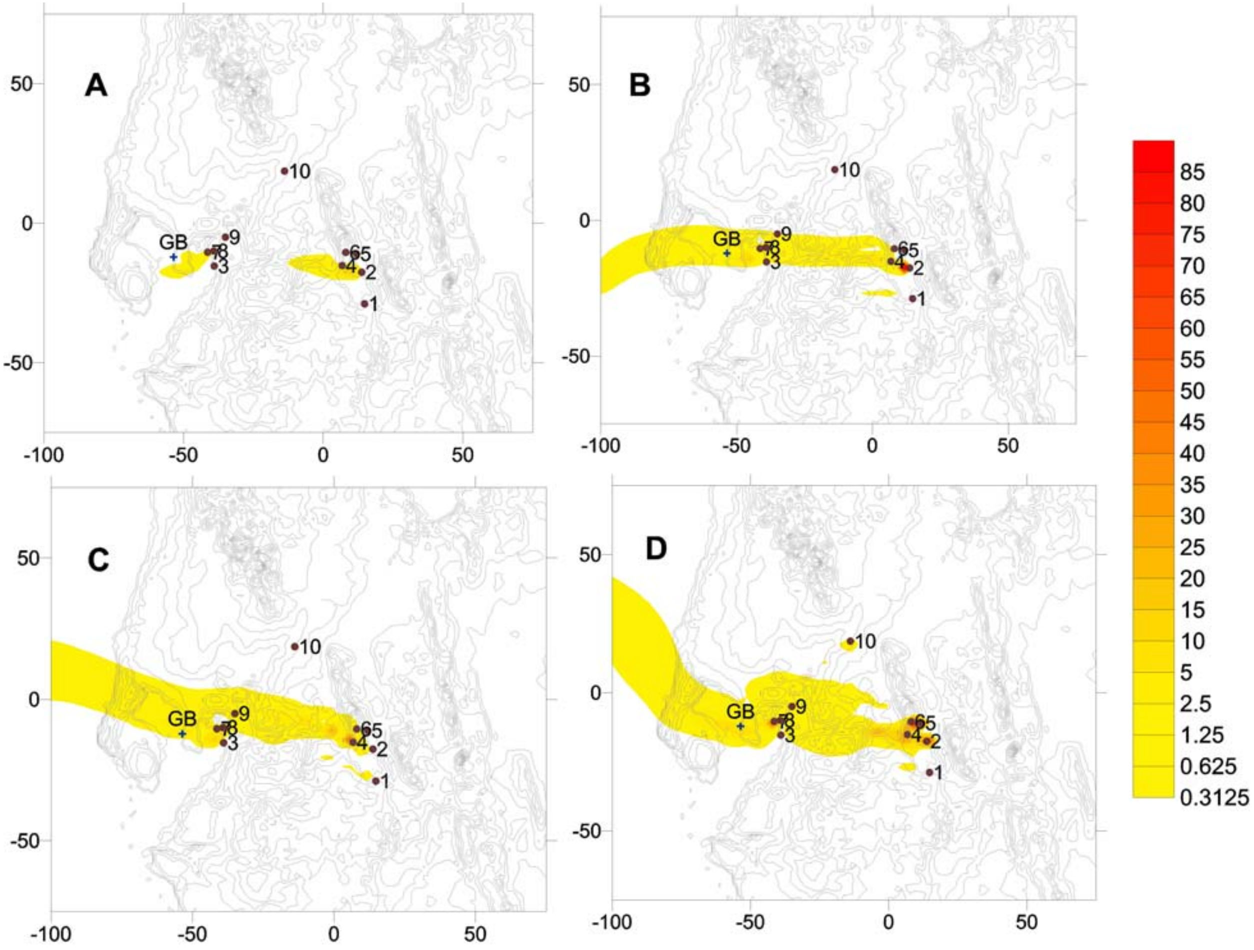

Fig. 2. Hourly average NH_3 concentrations from the fertilizer industry for 5/24/2004 at 1900 EST (A); for 5/24/2004 at 2200 EST (B); for 5/25/2004 0100 EST (C); and for 5/25/2004 (D). Also shown in the Gandy Bridge monitoring site (GB).

The atmospheric NH_3-N flux from all sources based on measured NH_3 concentrations at the Gandy Bridge site was 0.34 kg-N ha^{-1} mo^{-1} (35 Mt mo^{-1}), compared with 0.06 kg-N ha^{-1} mo^{-1} (6 Mt mo^{-1}) for the fertilizer industry. The latter deposition rate is ~10% of the total (wet + dry) direct atmospheric nitrogen deposition to Tampa Bay (Poor, et al., 2001). This rate could be high, because we did not take into account removal processes from point of emission; or low because we did not know the actual hourly emission rates; or either high or low because of poorly known stack parameters. Moreover, this dry deposition rate cannot be applied to all months of the year, because in the summer months with high rainfall, the rainfall scavenges NH_3 from the atmosphere and both air and water conditions favor the evasion of NH_3 from the bay rather than deposition to the bay (Mizak, 2004).

Conclusion

This brief study offers preliminary evidence that for May 2002 NH_3 emissions from the fertilizer industry contributed ~6 Mt of atmospherically-derived nitrogen to Tampa Bay. This evidence suggests that future control of this source category could help Tampa Bay “hold the line” on nitrogen loading.

Acknowledgements

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