Lessons Learned from the Bay Region Atmospheric Chemistry Experiment (BRACE) and Implications for Nitrogen Management of Tampa Bay

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Abstract

Results from air quality modeling and field measurements made as part of the Bay Region Atmospheric Chemistry Experiment (BRACE) along with related scientific literature were reviewed to provide an improved estimate of atmospheric reactive nitrogen (N) deposition to Tampa Bay, to apportion atmospheric N between local and remote sources, and to assess the impact of regulatory drivers on N deposition to Tampa Bay. Simulations using the Community Multiscale Air Quality model v4.4 modified with the University of California Davis aerosol module (CMAQ-UCD) provided a framework for this review. For 2002, CMAQ-UCD modeled atmospheric loading rates were 6,910 metric tons N to the land surface of the watershed and 548 metric tons N to bay surface of the watershed, respectively. If an 18% transfer rate of atmospherically-deposited N from watershed to bay is assumed, then the corresponding atmospheric loading to Tampa Bay was 1,790 metric tons N or 57 % of the total N loading to the bay. From CMAQ-UCD modeling, oxidized N sources both within and outside Tampa Bay's watershed were important contributors to atmospheric N loading to the bay. Within the watershed, oxidized N emissions from mobile sources had a disproportionally larger impact than did power plant sources on atmospheric N loading. Predicted decreases in atmospheric N deposition to Tampa Bay by 2010 due to regulatory drivers were significant, and plausibly evident in recent declines in ambient air NO_x concentrations in urban Tampa and St. Petersburg.

Keywords: Florida, atmospheric deposition, ammonia, nitrogen oxides, CMAQ-UCD

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1. Introduction

1.1 *Purpose and Scope*

Tampa Bay National Estuary Program (TBNEP) in 1996 published its nutrient budget for Tampa Bay, Florida, USA, which revealed that atmospheric deposition contributed ~ 67 % of the bay's total annual reactive nitrogen (N) loading (TBNEP, 1996). With the announcement in 1999 by a local utility company of its plans for significant reductions in power plant nitrogen oxide (NO_x) emissions, Tampa Bay Estuary Program (TBEP, formerly TBNEP) and Florida Department of Environmental Protection (FDEP) saw the need to model at a regional scale N emissions, transport, transformation, and deposition to assess the potential impact of these reductions on the bay's N budget. Bay Region Atmospheric Chemistry Experiment (BRACE) began in concept as a short-term "supersite" experiment intended to collect multi-dimensional meteorological and air pollution data to validate model performance, but evolved into a long-term multi-site experiment that included three intensive monitoring periods and several special studies (Atkeson et al., 2007). BRACE goals were to (1) improve estimates of atmospheric N deposition to Tampa Bay, (2) apportion atmospheric N between local, regional, and remote sources, and (3) assess the impact of utility controls on N deposition to Tampa Bay (Atkeson et al., 2007). The purpose of this article is to review BRACE modeling and measurement results with an emphasis on the results of CMAQ-UCD simulations, and to highlight the implications for bay management.

1.2 *Background*

Tampa Bay estuary is located along the west coast of central Florida and on Gulf of Mexico's eastern border (Figure 1), and at ~1,000 km^2 is Florida's largest open water estuary (Greening and Janicki, 2006). Three counties border directly on the bay: Pinellas, Hillsborough, and Manatee; Pasco, Polk, and Sarasota counties are also within the estuary's ~6,000 km^2 watershed (Figure 1). According to the 2010 US census, the population within

64 the bordering counties exceeded 2.5 million persons, with growth rates of more than 20%
65 seen in Hillsborough and Manatee counties between census years. Land use within the
66 watershed is mixed between undeveloped, agricultural, residential, commercial, and mining.
67 Tampa Bay's shipping trade and tourism, and to a lesser extent commercial and recreational
68 fishing, play an important role in the local economy (TBEP, 2006; Tomasko et al., 2005).
69
70 The subtropical bay is relatively shallow with an average depth of 4 m, although deeper
71 dredged channels allow large ships to reach three major seaports (TBEP, 2006). Mangrove
72 forests, salt marshes, and seagrass beds thrive along protected shorelines of Tampa Bay and
73 serve as nurseries for fish, shellfish, and crustaceans, and as a feeding ground for migratory
74 birds. Seagrasses are considered by scientists and estuarine managers to be a sensitive
75 indicator of the bay's overall health (TBNEP, 1996). Observations regarding the health of
76 seagrass beds is that inflows of bioavailable N cause excessive algal growth, which in turn
77 reduces water clarity and thus the ability of seagrass to survive in bay shallows (Sherwood,
78 2011). Between 1950 and 1985, seagrass acreage declined from 16,000 ha to 9,000 ha; bay
79 managers have set a recovery goal of 15,000 ha. The paradigm for recovery and maintenance
80 of seagrass is to reduce N inputs (Greening and Janicki, 2006; Greening et al., 2011).
81
82 In the mid-1990s, the Tampa Bay Estuary Program and its stakeholders set as a goal
83 reductions in loading of ~15 metric tons N yr^{-1} to maintain N loading at levels conducive to
84 seagrass growth even as the human population grew within the watershed (Greening et al.,
85 2011; Greening and Janicki, 2006). Through management actions, N inputs to Tampa Bay
86 were reduced. Between 1999 and 2010 in apparent response and concurrent to these
87 reductions, bay water clarity improved, chlorophyll α concentrations decreased, and seagrass
88 coverage steadily increased from 10,000 ha to 13,500 ha (Greening and Janicki, 2006;
89 Sherwood, 2011).
90
91 Bioavailable or reactive N reaches coastal ecosystems in stormwater runoff (62 %), direct
92 atmospheric deposition (21 %), point sources (12 %), groundwater springs (4 %), and
93 accidental fertilizer losses (1 %) (Greening and Janicki, 2006). Reactive nitrogen (N)
94 deposited from the atmosphere to the landscape that is subsequently transferred to the bay is

referred to as indirect atmospheric deposition or indirect loading and is included in the stormwater contribution. Atmospheric deposition of N can either directly or indirectly deliver much of the new N loading to a coastal embayment, with estimates between 9 % and 75 % of total N loading for bays of northeastern US (Howarth, 2008). Natural sources of atmospheric N include emissions from feral animal excreta, forest fires, lightning, oceans, soils, vegetation, and stratospheric injection; anthropogenic sources of N include emissions from fertilizer application to crops, from nitrogen-fixing crops, excreta from human and farm animal populations, urban fertilizer use, and fossil fuel combustion (Holland et al., 1999; Galloway et al., 2004; Howarth, 2008). Atmospheric deposition represents a major source of N to Tampa Bay and control of atmospheric emissions within and outside the watershed is important to the future of Tampa Bay estuary.

2. Modeling

2.1 *CMAQ-UCD modeling*

As part of BRACE, scientists modeled N transport, transformation, and deposition within the Tampa Bay watershed with the Models-3 Community Multiscale Air Quality (CMAQ) v4.4 modeling system (Dennis and Arnold, 2007; Nolte et al., 2008). CMAQ's chemical transport model simulates horizontal and vertical advection, horizontal and vertical diffusion, gas-phase and aqueous-phase reactions, cloud mixing and scavenging, aerosol dynamics, size distribution and chemistry, and wet and dry deposition of gases and aerosols to Earth's surface (Byun and Schere, 2006). Computations for wet deposition include in-cloud scavenging and below-cloud washout of air pollutants based on Henry's Law partitioning for gases and absorption of aerosols into cloud or rain water; dry deposition estimates assume turbulent transfer of gases and aerosols to the surface and resistance to gas transfer at the surface (Byun and Schere, 2006). CMAQ was run with University of California Davis (UCD) Aerosol Module to capture the dynamics of nitric acid (HNO_3) and sea salt interactions (Nolte et al., 2008; Zhang and Wexler, 2008); the UCD Aerosol Module is based on the Aerosol Inorganics Model (AIM) (Wexler and Clegg, 2002). This version of CMAQ is also known as CMAQ-UCD. Meteorological input to CMAQ-UCD was modeled with Fifth

Generation Penn State University/National Center for Atmospheric Research mesoscale model (MM5) v3.6 (Nolte et al., 2008).

Area source emissions were extracted from USEPA's 1999 national emission inventory (NEI) v3, projected to 2002 for mobile sources and to 2001 for other sectors. With slow economic growth, differences between the 2001 and 2002 inventories for other sectors is small. Emissions from electric generating units were based on 2002 continuous emission monitoring (CEM) data (Dennis and Arnold, 2007; Dennis et al., 2008). USEPA's ammonia (NH_3) inventory was adjusted upward to account for Florida's warmer wintertime temperature, and NH_3 deposition velocities were corrected downward by 30% from default values based on sensitivity studies conducted for Chesapeake Bay (Dennis et al., 2010; Dennis and Arnold, 2007). Biogenic sources from the Biogenic Emissions Inventory System (BEIS) v3.10 and size-segregated sea salt emissions, which were a function of wind speed and relative humidity, were input separately (Nolte et al., 2008).

Three nested grids were defined to bring the modeling scale to a size relevant to addressing deposition across Tampa Bay and its watershed. CMAQ-UCD's 32-km grid cell modeling domain covered the entire continental United States (US), within which was an 8-km nested grid cell size over southeastern US, and within which was a 2-km nested grid cell size over Tampa Bay's watershed and nearby regions (Dennis and Arnold, 2007). CMAQ-UCD simulations included meteorology for April, May, July, August, September, October, and November of 2002 and January, February, and March of 2003, to achieve a simulated rainfall amount that approximated the watershed's 15-year annual average (Dennis and Arnold, 2007). Months with unusually high or low rainfall were excluded. Annual accumulated wet and dry deposition was constructed from hourly deposition calculations over these ten months with an adjustment to account for the two missing months. CMAQ-UCD modeled reactive N species included reduced N: ammonia (NH_3) and ammonium (NH_4^+); and oxidized N: nitrogen monoxide (NO), nitrogen dioxide (NO_2), nitric acid (HNO_3), nitrate (NO_3^-), and other oxides of N generated from emissions of NO_x (= NO + NO_2) (Dennis and Arnold, 2007).

CMAQ model performance was evaluated against ground-based and aircraft meteorological and air pollutant measurements from BRACE (Arnold and Luke, 2007; Dennis and Arnold, 2007; Gunter, 2007; Luke et al., 2007a; Luke et al., 2007b; Nolte et al. 2008). Bias and error in MM5 meteorological modeling and CMAQ-UCD air pollutant modeling were judged typical of those seen in other CMAQ evaluations (Eder and Yu, 2006; Dennis and Arnold, 2007; Nolte et al., 2008). Atmospheric N deposition rates to Tampa Bay's watershed reported by Dennis and Arnold (2007) had a net positive bias of ~ 8 % relative to CMAQ simulations based on later updates made to NO, NO_2, and peroxyacetyl nitrate (PAN) deposition parameters.

2.2 *CALPUFF modeling*

The CALPUFF modeling system consists of three main components: CALMET, CALPUFF, and CALPOST (Scire et al., 2000). CALMET is a meteorological model that develops three-dimensional wind and temperature fields and two-dimensional fields for mixing height, surface characteristics, and dispersion properties. CALPUFF is a three-dimensional non-steady state Lagrangian puff model that simulates dispersion, transport, transformation, and removal through wet and dry deposition of air pollutants between 10s of m and up to hundreds of km from a source. CALPOST is a processes air pollutant concentrations and deposition fluxes from binary to text files. As part of BRACE, CALPUFF was employed (1) for source apportionment (Park et al., 2005; Poor et al., 2003), (2) to calculate gas and particle deposition velocities N and chloride (Poor et al., 2006) in support of an estimate of N retention in the Tampa Bay watershed (Pollman and Poor, 2003), (3) to determine intra-state transport of chloride as it related to partitioning of HNO_3 into sea salt (Dasgupta et al., 2007), and (4) to investigate the relationship between N emission and deposition for sources near to Tampa Bay (Poor, 2008). Details of CALMET and CALPOST model inputs and parameterizations can be found in the cited literature.

3. Results and Discussion

3.1 *How much of the total nitrogen loading to Tampa Bay is from atmospheric deposition?*

Poe et al. (2005), Pribble et al. (2001) and JEI (2008) estimated for 1999-2006 total N loading to Tampa Bay from direct atmospheric deposition, non-point sources, domestic and industrial point sources, springs, groundwater, and material losses (Figure 2). They calculated direct atmospheric deposition from monthly bay segment-specific rainfall rates, rainfall N concentrations, and seasonal dry:wet deposition ratios. Monthly rainfall N concentrations and seasonal dry:wet deposition ratios came from measurements made at National Atmospheric Deposition Program (NADP) Atmospheric Integrated Research Monitoring Network (AIRMoN) site FL 18 (Figure 1). Contributions from all other source categories were based in general on basin- or bay segment-specific measurements of stream, spring, and groundwater or wastewater discharges and their respective N concentrations; for sub-basins without either stream flow gauges or water quality measurements, an empirical model was applied to determine water discharge rates and N concentrations from monthly rainfall amount and seasonal run-off coefficients based on land use and soil type. TBNMC (2010) revised the point source and materials handling N loading rates used by Poe et al. (2005) and JEI (2008).

Total N loading to Tampa Bay varied from year to year, e.g., from 2,190 metric tons N in 2000 to 6,690 metric tons in 2003 (Figure 2). In 2003 and 2004, higher rainfall rates increased the hydrological loading within Tampa Bay's watershed, which increased N loading from non-point sources and in 2004 lead to emergency and accidental discharges of N from industrial point sources. CMAQ v4.7 modeling revealed that in years with less rainfall, atmospheric deposition of N within Tampa Bay's watershed was dominated by dry deposition (Poor et al., in review). Inter-annual estimates of direct atmospheric deposition N loading to total N loading have ranged from 14 % to 32 % and estimates of direct plus indirect atmospheric deposition N loading to total N loading have ranged from 35 % to 70 % (Figure 2; Poor et al., in review).

Other estimates of atmospheric loading rates to Tampa Bay ranged from 1,100 metric tons N yr^{-1} (Poor, 2008) to 3,030 metric tons N yr^{-1} (Dixon et al., 1996) as shown in Table 1 and were characteristic of an estuary and watershed with moderate N pollution (Dentener 2006;

Holland et al. 2005). The broad range in estimates suggested significant differences in measurement techniques, computational tools, and methodical assumptions. As examples, N deposition rates have been determined by a mass balance approach (Patwardhan and Donigian, 1997), bulk deposition monitoring (Dixon et al., 1996), ambient air and rainfall monitoring with inferential modeling of dry deposition velocities (Poor et al., 2001), wet deposition monitoring and use of dry-to-wet deposition ratios based on two years of local observations (Pribble et al., 2001; Poe et al., 2005; JEI, 2008), and fate and transport modeling (Appel et al., 2011; Dennis and Arnold, 2007; Poor, 2008). Fate and transport models have been diagnostic (Poor, 2008; Poor et al., 2006) and prognostic (Appel et al., 2011; Dennis and Arnold, 2007). Inventories for fate and transport models have been limited to central Florida (Poor, 2008) and inclusive of the entire US (Appel et al., 2011; Dennis and Arnold, 2007). Even within the same prognostic modeling framework, differences existed between spatial scales, parameterizations, and mechanistic algorithms (Appel et al., 2011; Dennis and Arnold, 2007).

Table 1. Summary of estimates for direct and indirect atmospheric deposition of reactive nitrogen (N) to Tampa Bay

Direct (metric tons N yr^{-1})	Indirect (metric tons N yr^{-1})	Year(s) modeled/measured	References
1,800	1,210	1984-1987	Patwardhan & Donigian, 1997
1,240	1,790	1985-1991	Dixon et al., 1996
1,000	-	1995-1998	Pribble et al., 2001
760	-	1996-1999	Poor et al., 2001
840	-	2002	Poe et al., 2005
-	1,750[a]	2002-2003	Poor et al., 2006
550	1,240[a]	2002-2003	Dennis and Arnold, 2007
480	620[a]	2002	Poor, 2008
1,080	1,490[a]	2002	Poor et al. (in review)

[a]18% transfer coefficient applied to estimate of terrestrial loading within watershed

CMAQ-UCD modeling yielded for 2002 atmospheric loading rates of 6,910 metric tons N to land and 548 metric tons N to the bay (Dennis and Arnold, 2007). Assuming 18% of

atmospherically-deposited N was transferred from watershed to bay (Pollman and Poor, 2003) the estimated annual atmospheric loading to Tampa Bay was 1,790 metric tons N. Dennis and Arnold (2007) reported that of this 1,790 metric tons N loading, relative contributions were 60 % and 40 % for oxidized and reduced N, respectively, and 67 % and 33 % for dry and wet N deposition, respectively.

Poe et al. (2005) estimated that for 2002, total loading to Tampa Bay was 3,420 metric tons N of which 840 metric tons N, or 25 % came directly from the atmosphere. To create an estimate of the indirect loading from atmospheric deposition to the watershed, we revised the 2002 total loading figure by our new estimate of direct atmospheric deposition (Table 1) as 3,420 – 840 + 550 = 3,130 metric tons N and assumed that the indirect atmospheric deposition was included in the non-point source contribution to total N loading. The CMAQ-modeled contribution of atmospheric N loading to total N loading was 1,790 ÷ 3,130 = 57 %, of which 17 % was from direct and 40 % was from indirect deposition (Dennis and Arnold, 2007). The CMAQ-UCD model estimates were on the lower end of the direct loading range and in the middle of the indirect loading range (Table 1).

Some of the differences seen between estimates shown in Table 1 were attributed to measurement error. For example, a significant source of measurement error in the estimates described by Poor et al. (2001) was the loss of HNO_3 at the inlet to the annular denuder system for both cyclone and elutriator inlets, as compared with other field-based HNO_3 measurement methods (Arnold et al., 2007; Poor et al., 2006). These losses could bias ~ 50 % low the HNO_3 dry deposition rates (Figure 3). A second source of measurement error, also associated with the annular denuder system, was the use of an inlet with a fine particle cut-point. The inlet was designed to remove from the atmosphere with 50 % efficiency those particles with an aerodynamic diameter of 2.5 μm, and with increasing efficiencies for smaller particles. NO_3^-, however, was present in the atmosphere as a coarse particle distributed in diameter around a ~ 4-μm mode (Campbell et al., 2002; Evans et al., 2004). As illustrated in Figure 4, the use of the $PM_{2.5}$ cut-point could bias ~ 60 % low the nitrate particle deposition rates (Campbell et al., 2003).

Poor et al. (2001) applied the NOAA buoy model to calculate overwater dry deposition velocities. Meteorological input to this model was obtained from an overwater station (Mizak et al., 2007; Sopkin et al., 2006). Sopkin et al. (2006) compared the performance of the NOAA buoy model and the Tropical Ocean Global Atmosphere (TOGA) Coupled-Ocean Atmospheric Response Experiment (COARE) for predicting sensible heat and friction velocities from overwater meteorological measurements. They found that while both models tended to under-predict sensible heat, which would likely result in an under-prediction of deposition velocities, modeled results for the statistical tests employed were still within recommended performance guidelines. Their results had the caveat that neither model predicted well for periods when the atmosphere was stable.

The CMAQ simulation did not consider organic N deposition. Wet deposition estimates by Poor et al. (2001) were biased at least 10% low without the inclusion of organic N. Organic N compounds such as urea, aliphatic amines and amino acids, pesticides, and nitrate-substituted organics (e.g., peroxyacetyl nitrate) added to atmospherically-deposited N. Calderón et al. (2007) estimated that organic N made up ~10 % and ~9 % of the total dissolved nitrogen in PM_{10} and in rainfall, respectively, and that most of the aerosol organic N was in the fine particle fraction (Calderón et al., 2006).

CMAQ-UCD modeling showed steep atmospheric N deposition gradients and relatively high contributions of local oxidized N emissions to gradients associated with urban development and industrial activity near the bay (Dennis and Arnold, 2007). Atmospheric N deposition gradients for reduced N emissions were steep in the vicinity of industrial activity within the watershed (Poor et al., in review). Ambient air monitoring across Tampa Bay's watershed revealed that a significant spatial gradient existed between urban and rural sites for oxidized N but not reduced N concentrations (Poor et al., 2006). Inconsistent results between CMAQ-UCD modeling and local measurements of reduced N were likely a consequence of the limited number and placement of monitors, which emphasizes the importance of both modeling and measurement.

For CMAQ-UCD simulations (Dennis and Arnold, 2007), average wet oxidized N

deposition rates were lower and dry reduced N deposition rates higher than for CMAQ v4.7 simulations (Appel et al., 2011; Poor et al., in review) (Table 2). CMAQ-UCD simulations, however, were tailored for the Tampa Bay watershed and featured a grid cell size of 2 km x 2 km versus 12 km x 12 km for CMAQ 4.7. A finer scale grid cell size improved the resolution of land-sea breezes and mitigated error associated with sub-grid heterogeneity (Luke et al., 2007b). For CMAQ-UCD modeling an upward adjustment was made to the NH_3 emissions inventory to account for the warmer year-round temperatures in subtropical Florida. Neither the CMAQ-UCD nor the CMAQ v4.7 simulations included NO_x generated from lightning or bi-directional NH_3 exchange at the earth's surface, which may have biased estimates low (Appel et al., 2011).

Table 2. Comparison of average annual N atmospheric deposition rates between CMAQ-UCD and CMAQ v4.7 model simulations with 2002 meteorology.

Form of N	CMAQ v4.7		CMAQ –UCD*	
Deposition	Land, kg N ha^{-1}	Bay, kg N ha^{-1}	Land, kg N ha^{-1}	Bay, kg N ha^{-1}
Dry Oxidized N	6.29	5.23	6.08	2.07
Wet Oxidized N	3.64	3.24	1.64	1.84
Dry Reduced N	1.66	0.887	3.36	1.39
Wet Reduced N	2.15	1.53	1.60	1.42
Total	13.7	10.9	12.7	6.71

*Developed from CMAQ v4.4

3.2 What sources or source categories contribute the most to atmospheric deposition of nitrogen to Tampa Bay?

Release scenarios for power plant plumes are quite different from mobile source plumes. Power plant plumes near their exhaust stack are concentrated and lofted and plume touch down at the surface may occur many km distant from the plant. Figure 5, for example, shows measured oxidized N and other constituents in power plant plumes that swept across monitors at an air pollution monitoring site on the eastern fringe of Tampa's metropolitan area (Park et al., 2005; Poor et al., 2003). Power plant emissions greatly influence regional

transport of pollutants (Pinder et al., 2008; Strayer et al., 2007). Motor vehicles release their exhaust near the surface; emissions from roadway traffic are rapidly diffused and difficult to discern from "background" concentrations within a km from a roadway (Cape et al., 2004; Kenty et al., 2007). Nonetheless, emission sources near the surface such as mobile sources can dominate local deposition (Dennis and Arnold, 2007).

Luke et al. (2003) presented their initial oxidized-N flux (emission) estimates for the metropolitan area surrounding Tampa Bay from aircraft measurements of atmospheric constituents (Luke et al., 2007a, 2007b). Daily fluxes were calculated from five flights in May 2002 as the product of the wind speed and N concentration (less "background") and integrated across the cross-sectional area of the urban plume. Their average oxidized N flux was 470 metric tons d^{-1} and included point, area, and mobile source emissions.

By comparison, CMAQ-UCD modeled 2002 NO_x emissions for Tampa Bay's watershed were ~360 metric tons d^{-1} (130,000 metric tons yr^{-1}), distributed as 25 % from mobile sources, 50 % from power plants, and 25 % from other sources (Dennis and Arnold, 2007). Based on a CMAQ-UCD sensitivity analysis to assign attribution for the oxidized-N deposition, approximately 50 % of the oxidized-N atmospheric deposition to the Tampa Bay watershed came from NO_x emissions from within the watershed and 50 % from NO_x emissions outside the watershed. Over the Tampa urban core NO_x emissions from within the watershed were responsible for more than 80 % of the oxidized-N deposition, a highly localized result that also applies to St. Petersburg. Of the oxidized N deposition directly to the bay, approximately 42 % was due to NO_x emissions from within the watershed and 58 % from NO_x emissions outside the watershed because wet deposition plays a larger role in deposition to the bay.

Strayer et al. (2007) estimated from trends in local rainwater chemistry that oxidized and reduced N emission sources within central Florida contributed at least 25 % of the ~ 4 kg N ha^{-1} yr^{-1} delivered annually in rainfall to the surface of Tampa Bay. Their conclusion was supported by CMAQ-UCD modeling predicted an average wet deposition of 3.26 kg N ha^{-1} yr^{-1} (Table 2) to the surface of Tampa Bay, to which watershed mobile, power plant, and

other sources contributed 8.8 %, 18.5 %, and 12.4 %, respectively, or 1.3 kg N ha^{-1} yr^{-1} (Dennis and Arnold, 2007).

Mobile source emissions released near the surface and power plant emissions released from tall stacks did not have the same degree of responsibility for local deposition. For the half of the oxidized-N deposition to the watershed due to NO_x emissions from within the watershed the responsibility was distributed as 47 % from mobile sources, 27 % from power plants, and 25 % from other sources (Dennis and Arnold, 2007). For direct deposition to the bay that was attributable to local sources the relative responsibilities were comparable. The CMAQ-UCD sensitivity results suggested that, per unit of emission, over the watershed the mobile NO_x emissions were responsible for four times more oxidized-N deposition than the power plant emissions and over the bay the mobile NO_x emissions were responsible for twice as much oxidized-N deposition as the power plants. Thus, mobile sources had a disproportionately higher contribution than power plant sources to atmospheric N deposition to Tampa Bay.

From the USEPA's 2002 NEI v3 (USEPA, 2008), within the Tampa Bay watershed anthropogenic NO_x (as N) emissions were ~ 10 times greater than the NH_3 (as N) emissions, yet CMAQ-modeled oxidized N and reduced N contributed approximately 60 % and 40 %, respectively, of the N deposited to Tampa Bay and its watershed (Dennis and Arnold, 2007). The relative importance of reduced N to atmospheric N deposition is explained by transport of NH_3 into the watershed (Dennis et al., 2010), higher deposition velocities of NH_3 versus NO_x, (Dennis et al., 2010: Myles et al., 2007; Poor et al., 2006), and the near surface emissions of the NH_3 inventory compared with a combination near surface and elevated emissions for the NO_x inventory. Inventoried NH_3 emissions in the Tampa Bay watershed, for example, were predominantly from on-road sources or concentrated animal feed operations. Both CMAQ-UCD and CALPUFF modeling results suggested that reducing mobile source emissions within the watershed had a leveraged impact on reducing N deposition to Tampa Bay (Dennis and Arnold, 2007; Poor, 2008).

3.3 What are the temporal trends in atmospheric nitrogen deposition?

Through Clean Air Interstate Rule (CAIR, replaced with Cross-State Air Pollution Rule), Tier 2 Vehicle and Gasoline Sulfur Rules, Heavy Duty Highway Rule, and Non-Road Diesel Rule (USEPA, 2011a, b), USEPA seeks to improve air quality by phased reductions in air pollutant emissions from both fixed and mobile sources. Fully implemented, these regulations remove 6.7 million metric tons of NO_x emissions from all states in continental US, of which 5.2 million metric tons are from states in eastern US (Houyoux, 2005). On-road sources comprised 77 % and 74 % of the NO_x emissions reductions for continental and eastern US, respectively (Houyoux, 2005). NO_x regulatory drivers do not address NH_3 emissions, so these emissions are anticipated to grow with agricultural demand. Estimates are that NH_3 emissions are expected to grow by 0.44 million metric tons for all states in continental US, of which 0.22 million metric tons of NH_3 emissions are from states in eastern US (Houyoux, 2005). Moreover, slated reductions in sulfur dioxide (SO_2) emissions will shift aerosol NH_4^+ to gaseous NH_3 and thus favor increased localized deposition of reduced N (Pinder et al., 2008).

CMAQ-UCD modeling was conducted to assess the potential impact of the CAIR by 2010 on atmospheric N deposition to Tampa Bay and its watershed. CMAQ-UCD modeling of the 2010 CAIR NO_x emissions inventory (Houyoux, 2005) showed a removal of 390 metric tons N or a 390/1,790 = 22 % reduction for atmospheric N loading to the bay (Dennis and Arnold, 2007), assuming an 18% transfer rate from watershed to bay. Poor et al. (in review) reported a 33% percentage reduction in atmospheric N deposition based on CMAQ v4.7 modeling of the CAIR impact through 2020 (Appel et al., 2011). Reconfiguration of two local coal-fired power plants between 2002 and 2010 accounted for 86 metric tons N of this reduction in N deposition (Dennis and Arnold, 2007).

Was a downward trend seen in measured wet and dry N deposition rates? Between 1997 and 2011, NH_4^+ and NO_3^- rainfall concentrations and deposition rates determined from weekly rainfall collected at NADP's National Trends Network (NTN) site FL 41 (Figure 1; NADP, 2011) in Sarasota County did not discernibly track downward with reductions in emissions from Florida power plants (Figure 6; USEPA, 2011). The apparent downward

trend in NO_3^- deposition rates was not statistically significant for inference testing of log-transformed data at the 95% confidence level. The lack of a significant downward trend in observed NO_3^- wet deposition rates was a likely consequence of the location of rainfall monitoring relative to major NO_x sources, especially urban mobile sources, "smearing" of storm events during rainfall collection, a relatively low contribution of local oxidized N sources to rainfall NO_3^-, and low statistical power given the variability and dispersion of rainfall rates (Mizak et al., 2005; Strayer et al. 2007; Dennis and Arnold 2007).

No measured dry N deposition rates were available over the same period but ambient air NO_x concentrations observed at urban monitors in both Hillsborough and Pinellas counties tracked downward with reductions in emissions from Florida power plants (Figure 7; USEPA, 2011). The downward trend in NO_x concentrations were statistically significant based on inference testing of log-transformed data at the 95% confidence level and offered evidence in support of CMAQ-UCD modeled predictions of lower N deposition rates.

3.4 Implications for Tampa Bay Estuary

Algal abundance, water clarity, and seagrass acreage have improved substantially in the Tampa Bay estuary between 1999 and 2010 (Sherwood, 2011) and it appears plausible that declines in atmospheric N deposition to the estuary and its watershed were part of this historical improvement. Estimates from both modeling and measurement revealed that since the mid-1980s atmospheric N deposition to Tampa Bay has been a significant fraction of its annual N loading. Further reductions in atmospheric N deposition are essential if only to "hold the line" against population growth with its attendant reduced and oxidized N emission sources. Air quality modeling has illustrated for us that any successful strategy to "hold the line" must include components of both local and regional air quality control, ammonia (NH_3) and well as NO_x control, and non-point as well as point source emission control. CMAQ-UCD simulations indicated that implementation of regulatory drivers between 2002 and 2010 represented a decrease of ~49 metric tons N yr^{-1}, well above a target reduction rate of 15 metric tons N yr^{-1} needed to maintain a bay water quality for healthy seagrass beds (Greening et al., 2011; Greening and Janicki, 2006).

4. Summary and Conclusions

What are the lessons learned from the BRACE? First, atmospheric N deposition is a significant fraction of Tampa Bay's total N loading, with estimates of inter-annual direct atmospheric N deposition between 14 % and 32 %, and total (direct plus indirect) atmospheric N deposition between 35 % and 70 %. Second, based on CMAQ-UCD modeling of atmospheric N deposition, the relative contributions of oxidized N and reduced N were 60 % and 40 %, respectively, and the relative contributions of dry and wet N deposition were 67 % and 33 %, respectively, to atmospheric N loading. Ideally, the relative importance of reduced N, dry N, and atmospheric N loading to total N loading to Tampa Bay would be reflected in watershed monitoring. Third, modeled N mobile source emissions, which are released close to the watershed surface, had a disproportionally larger impact than did power plant emissions on oxidized N deposition to Tampa Bay and its watershed. Thus, reductions in N emissions from mobile sources must be a part of the strategic plan for reducing N loading to the bay. Fourth, modeled NO_x emissions within the watershed contributed to 50 % of the oxidized-N deposition to the watershed and 42 % of the oxidized-N deposition to the bay. CMAQ-UCD modeling predicted a ~ 22 % decrease in atmospheric N deposition by 2010 due to regulatory drivers, which is plausibly in evidence by corresponding declines in NO_x concentrations in urban Tampa and St. Petersburg. Control of atmospheric N emissions both within and outside the watershed is important to the future of the Tampa Bay estuary.

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approved for publication, it may not necessarily reflect official Agency policy. Mention of commercial products does not constitute endorsement by the Agency.

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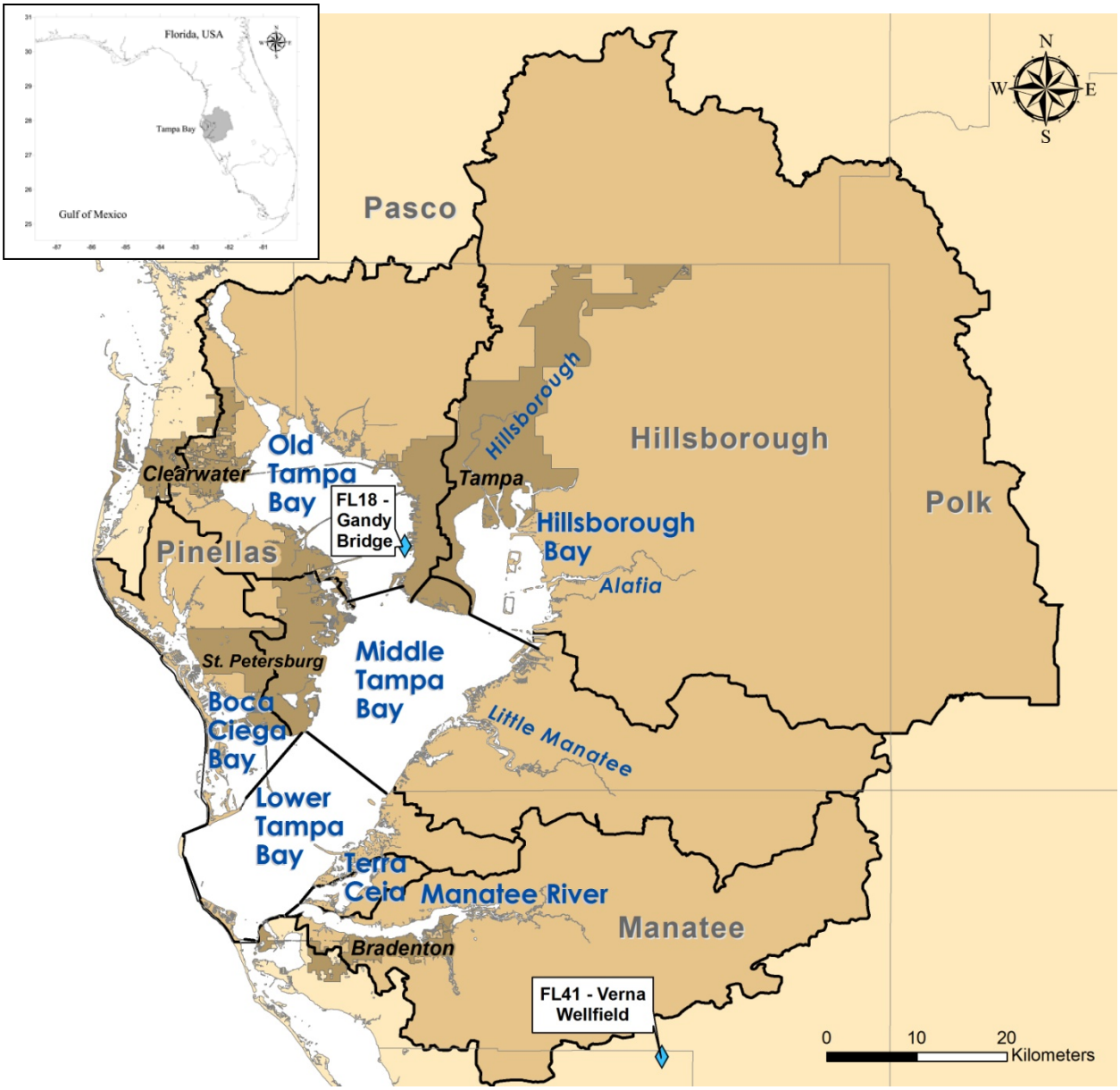

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742 **Figure 1.** Tampa Bay and its watershed. Also shown are the National Atmospheric
743 Deposition Program (NADP) National Trends Network (NTN) wet deposition monitoring
744 site at Verna Wellfield in Sarasota Count, the NADP Atmospheric Integrated Research
745 Monitoring Network (AIRMoN) site FL 18.

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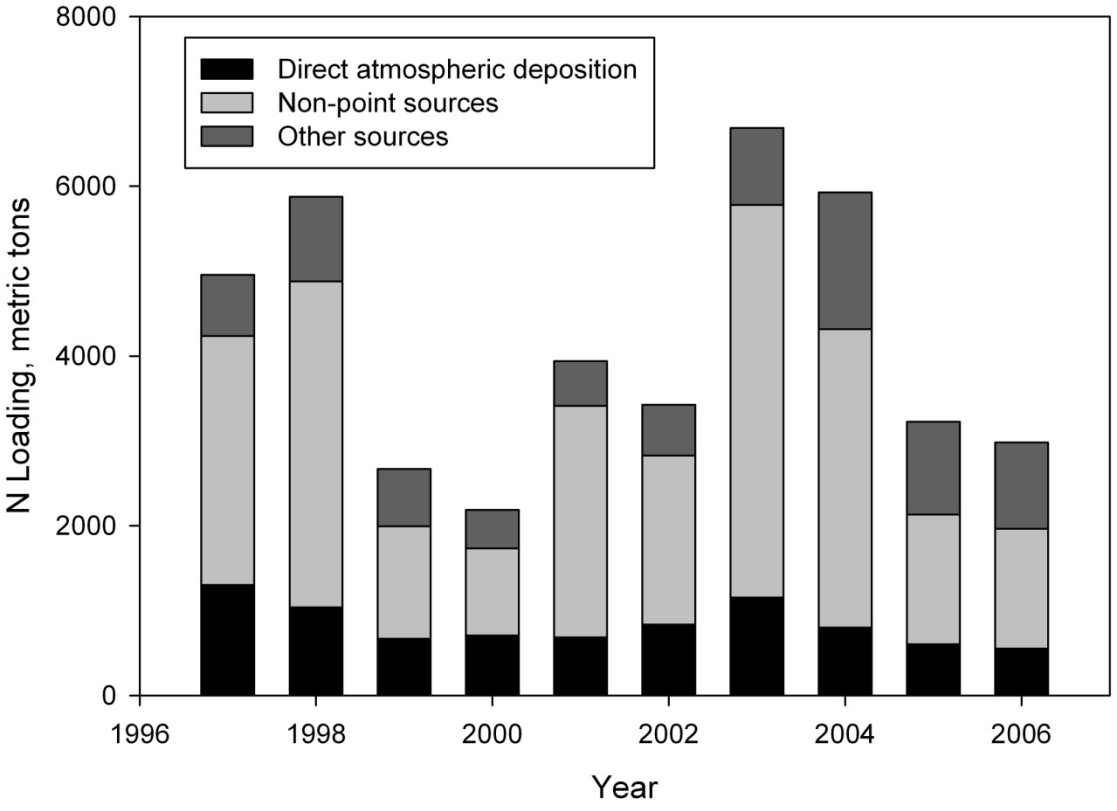

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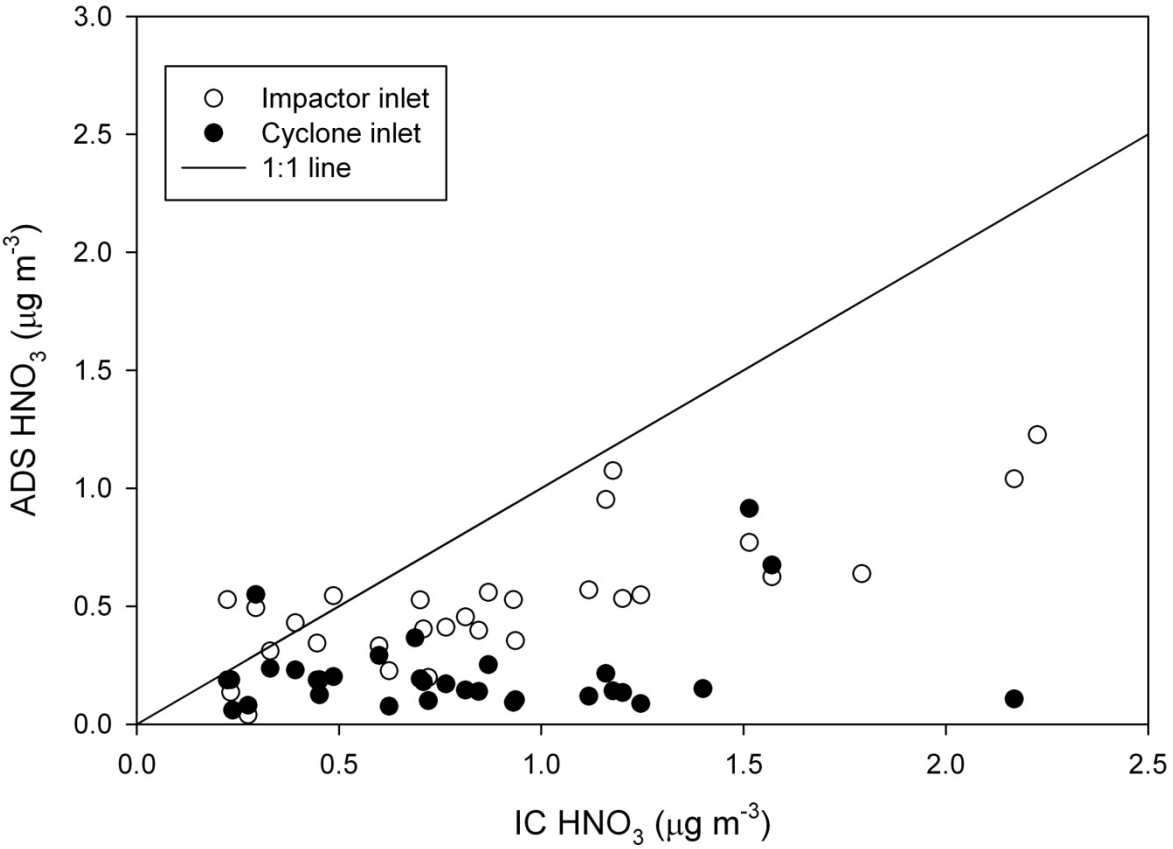
749 **Figure 2.** N loading rates to Tampa Bay by source category. Indirect atmospheric deposition
750 in included as a non-point source; other sources include domestic and industrial point
751 sources, springs, groundwater, and material losses (JEI, 2008; Poe et al., 2005; Pribble et al.,
752 2001; TBNMC, 2010).



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755 **Figure 3.** Comparison of annular denuder system (ADS) measurements of HNO_3 made with
756 either a cyclone or impactor inlet versus ion chromatography (IC) measurements of HNO_3
757 made with a short straight tube for an inlet.

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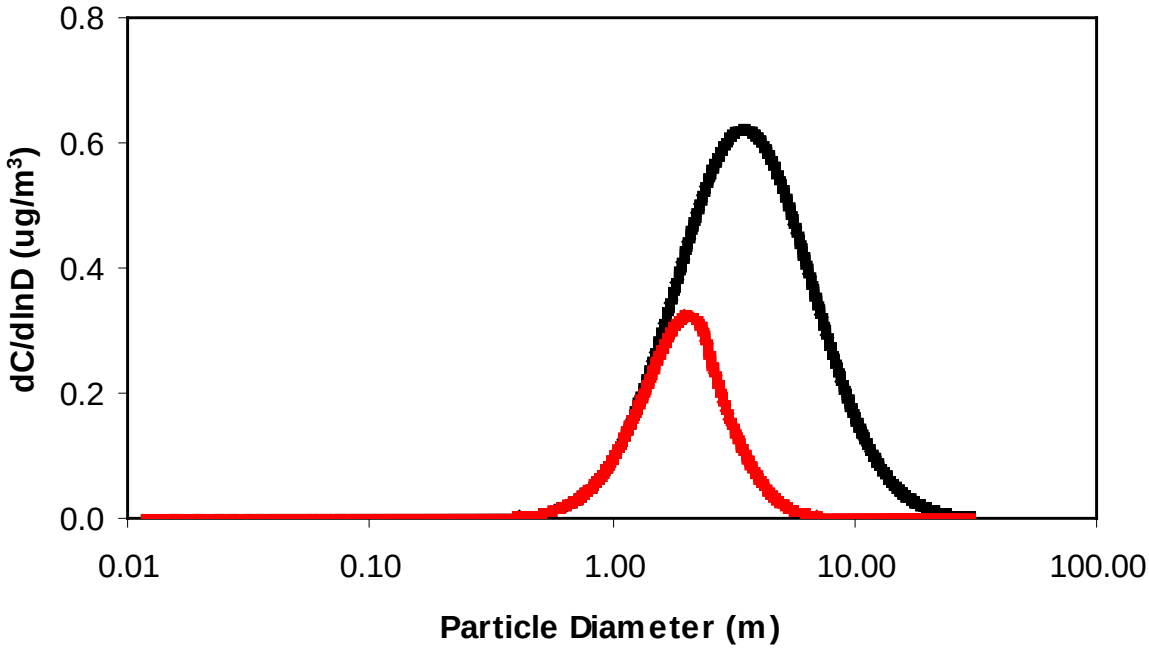

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760 **Figure 4.** Comparison of NO_3^- aerosol distribution obtained with a micro-orifice impactor
761 (MOI) (tall curve) and fraction of this distribution captured by an annular denuder system
762 (ADS) (short curve). The MOI had an inlet with a coarse particle cut-point; the ADS had an
763 inlet with a fine particle cut-point.

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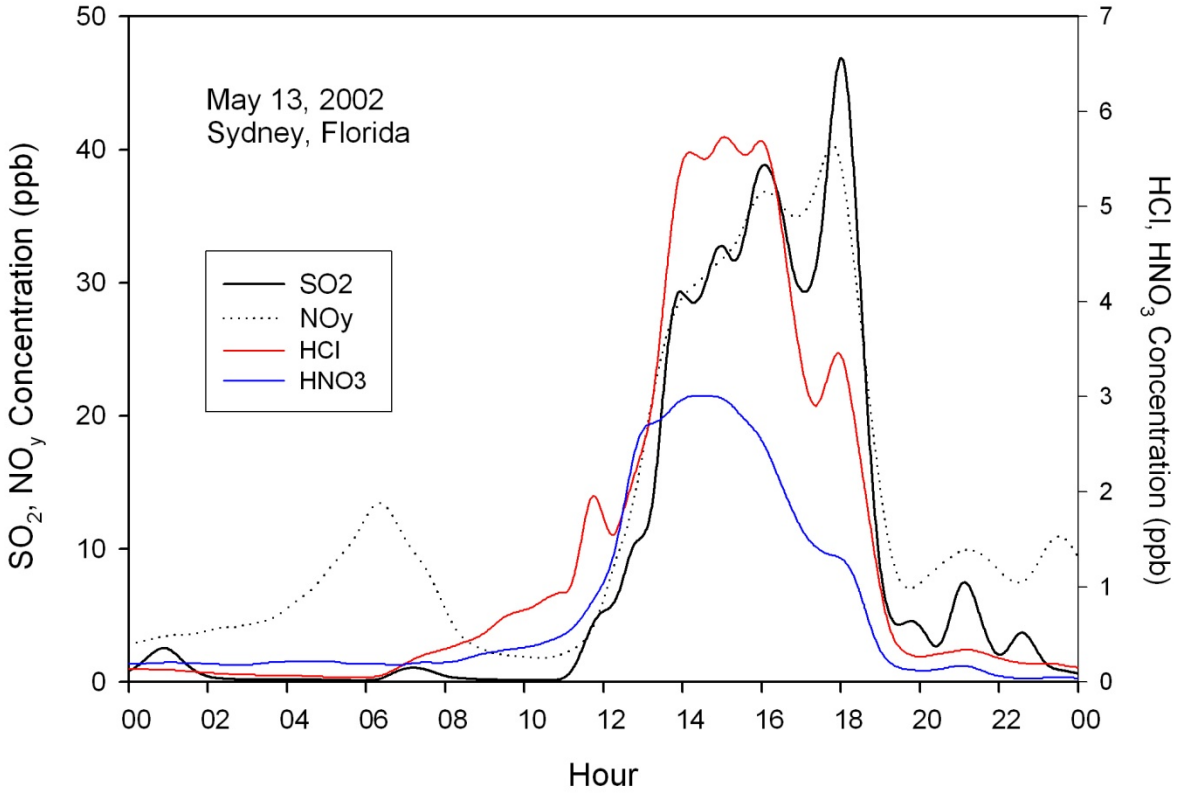

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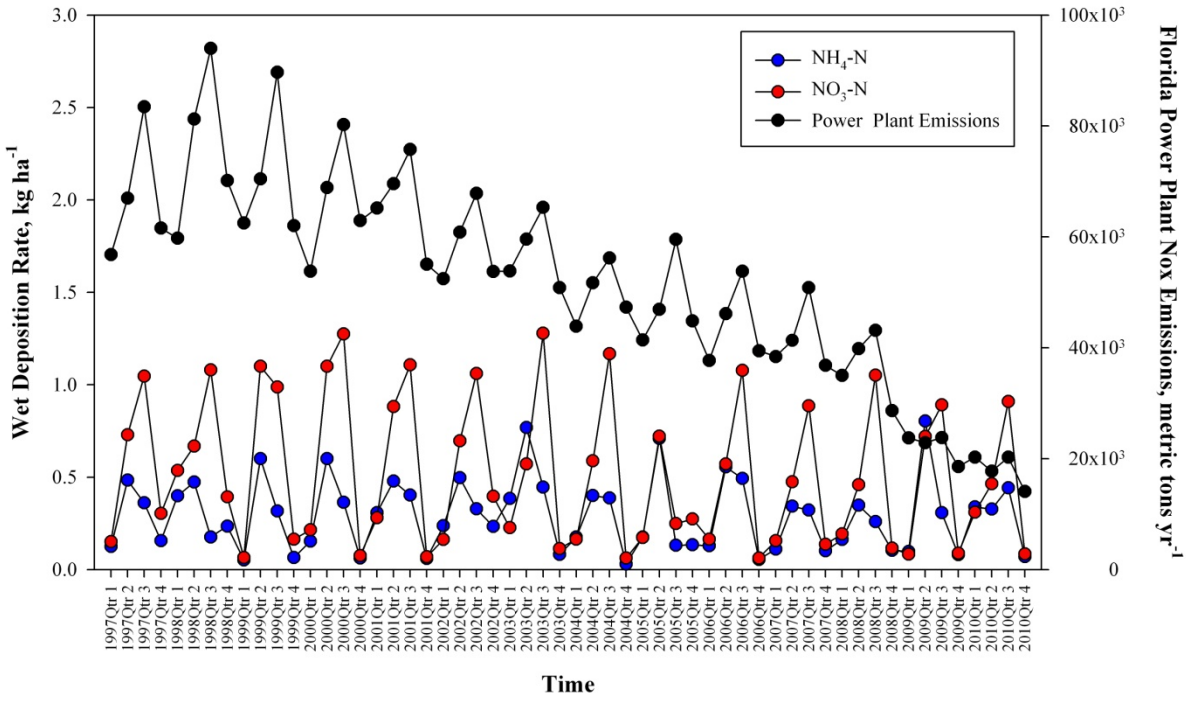
767 **Figure 5.** Time-dependent concentrations of air pollutants measured at an air

768 pollution monitoring site near Sydney, Florida, on May 13, 2002.



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770 **Figure 6.** Trends in quarterly Florida power plant NO_x emissions and N wet deposition rates

771 at NADP's Verna Wellfield monitoring site, Sarasota County, Florida.

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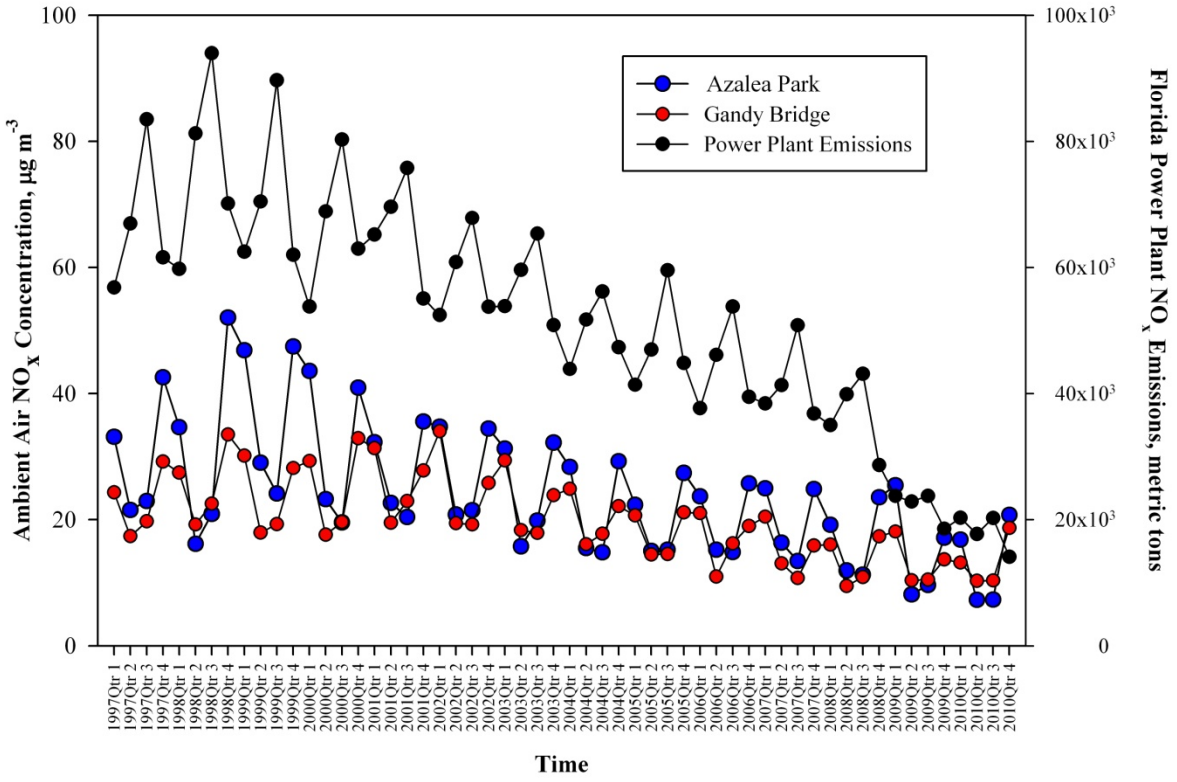

773

774 **Figure 7.** Trends in quarterly Florida power plant NO_x emissions and ambient air NO_x

775 concentrations at Gandy Bridge and Azalea Park monitoring sites in Tampa and St.

776 Petersburg, Florida, respectively.

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778