- 1 Application of Watershed Deposition Tool to Estimate from CMAQ
- 2 Simulations the Atmospheric Deposition of Nitrogen to Tampa Bay and Its
- 3 Watershed

- 5 Noreen Poor
- 6 Kivmetrics, LLC, 4600 Explorer Dr., No. 102, West Melbourne, FL 32904

7

- 8 Ray Pribble
- 9 Janicki Environmental, Inc., 1155 Eden Isle Dr., NE, St. Petersburg, FL 33704

10

- 11 Donna Schwede
- 12 U. S. Environmental Protection Agency, National Exposure Research Laboratory, Atmospheric
- 13 Modeling and Analysis Division, Research Triangle Park, NC 27711

14

15 ABSTRACT

- 17 The USEPA has developed Watershed Deposition Tool (WDT) to calculate from the Community
- 18 Multiscale Air Quality (CMAQ) model output the nitrogen, sulfur, and mercury deposition rates
- 19 to watersheds and their sub-basins. The CMAQ model simulates from first principles the
- 20 transport, transformation, and removal of atmospheric pollutants. We applied WDT to estimate
- 21 the atmospheric deposition of reactive nitrogen (N) to Tampa Bay and its watershed. For 2002
- 22 and within the boundaries of Tampa Bay's watershed, modeled atmospheric deposition rates
- 23 averaged 13.3 kg N ha⁻¹ yr⁻¹ and ranged from 6.24 kg N ha⁻¹ yr⁻¹ at the bay's boundary with Gulf
- of Mexico to 21.4 kg N ha⁻¹ yr⁻¹ near Tampa's urban core, based on a 12-km x 12-km grid cell
- size. CMAQ-predicted loading rates were 1,080 metric tons-N yr⁻¹ to Tampa Bay and 8,280
- 26 metric tons-N yr⁻¹ to the land portion of its watershed. If we assume a watershed-to-bay transfer
- 27 rate of 18 % for indirect loading, our estimates of the 2002 direct and indirect loading rates to
- 28 Tampa Bay were 1,080 metric tons-N and 1,490 metric tons-N, respectively, for an atmospheric
- 29 loading of 2,570 metric tons-N or 71 % of the total N loading to Tampa Bay. To evaluate the
- 30 potential impact of USEPA's Clean Air Interstate Rule (CAIR, replaced with Cross-State Air
- 31 Pollution Rule), Tier 2 Vehicle and Gasoline Sulfur Rule, Heavy Duty Highway Rule, and Non-

Road Diesel Rule, we compared CMAQ outputs between 2020 and 2002 simulations, with only
the emissions inventories changed. CMAQ-projected change in atmospheric loading rates
between these emissions inventories was 857 metric tons-N to Tampa Bay, or about 24 % of the
2002 total N loading to Tampa Bay from all sources.

IMPLICATIONS

Air quality modeling reveals that atmospheric deposition of reactive nitrogen (N) contributes a significant fraction to Tampa Bay's total N loading from external sources. Regulatory drivers that lower nitrogen oxide emissions from power plants and motor vehicles are important to bay management strategies, which seek to improve water quality through N load reduction.

INTRODUCTION

Tampa Bay is a 100,000-ha subtropical, shallow, tidal estuary on the western coast of central Florida and eastern side of Gulf of Mexico. Land use in Tampa Bay's 600,000-ha watershed is predominantly urban in its western and northern sectors, agricultural in its southern and eastern sectors, and industrial in ports on the bay's coastline (Figure 1). Fluxes of reactive nitrogen (N) to the bay and recycling of accumulated nutrients within the bay contribute to algal blooms, which shade the water column and create conditions that are unfavorable for sea grasses (Conley et al., 2009; Greening et al., 2011; Wang et al., 1999). Sea grasses are important to the estuary as a nursery for fish and shellfish and for their ability to retain sediment (Greening et al., 2011). The bay management strategy seeks to reduce N inputs and to re-establish lost sea grass beds (Greening and Janicki, 2006). Through management actions, N inputs have been reduced. The success of this strategy is evidenced by improved water clarity, lower chlorophyll α concentrations, and expansion of seagrass acreage in apparent response to significant reductions in N loading to Tampa Bay (Conley et al., 2009; Greening and Janicki, 2006; Sherwood, 2010).

New N enters Tampa Bay from non-point sources (62 %), direct atmospheric deposition (22 %), point sources (12 %), groundwater discharge (4 %), and accidental fertilizer losses (1 %) (Greening and Janicki, 2006). Atmospheric N that deposits first to land surface within the

watershed and then moves either with stormwater runoff or via groundwater to the bay is referred to as indirect atmospheric deposition and is a non-point source. From the above percentages, between 22 % and 84 % of the new N reaching Tampa Bay is from atmospheric N deposition. Reductions of atmospheric contributions to N loading are important to achieving bay water quality goals.

Measurements of atmospheric N deposition near Tampa Bay are scarce. Therefore, air quality modeling is an important source of deposition estimates and for assessments of the change in deposition due to changes in emission inventories. The Community Multiscale Air Quality (CMAQ) model simulates from first principles the transport, transformation, and removal of atmospheric pollutants (Byun and Schere, 2006). The USEPA has developed the Watershed Deposition Tool (WDT) to calculate from the CMAQ model output N, sulfur, and mercury deposition rates to watersheds and their basins (Schwede et al., 2009). Figure 2, for example, shows WDT's display for annual atmospheric N deposition by basins and bay segments within Tampa Bay's watershed for 2002.

We applied WDT to estimate the atmospheric deposition of N to Tampa Bay and its watershed, to look at temporal trends in N deposition, and to evaluate the aggregate impact to Tampa Bay of the USEPA's health-driven regulatory drivers associated with the 1990 CAA. CMAQ-modeled and measured monthly wet N deposition rates were compared for a National Atmospheric Deposition Program (NADP) site near the southern boundary of Tampa Bay's watershed.

EXPERIMENTAL METHODS

CMAQ Modeling

CMAQ v4.7 chemical transport model simulated horizontal and vertical advection, horizontal and vertical diffusion, gas-phase and aqueous phase reactions, cloud mixing, aerosol dynamics, size distribution and chemistry, and deposition of gases and aerosols to Earth's surface (Byun and Schere, 2006; Schwede et al., 2009). CMAQ v4.7 included revisions to the cloud model, improvements to treatment of secondary organic aerosols and dinitrogen pentoxide (N₂O₅)

parameterization, and added dynamic mass transfer for coarse-mode aerosols, as examples (Foley et al., 2010). Computations for wet deposition included in-cloud scavenging and below-95 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 assumed turbulent transfer of gases and aerosols to the surface and resistance to gas transfer at the surface (Byun and Schere 2006; 98 Schwede et al. 2009). We used CMAQ v4.7 model simulations for 2002 – 2006 from Appel et al. (2011) that had been post-processed for the WDT. For these simulations, the modeling domain covered the 102 103 eastern 2/3 of United States (US), southern Canada, and northern Mexico, with a 12-km x 12-km 104 grid cell size and where boundary conditions were provided by a separate 36-km x 36-km continental US simulation (Appel et al., 2011; Foley et al., 2010). Year-specific meteorology 105 106 was modeled with the Fifth Generation Penn State University/ National Center for Atmospheric Research (NCAR) mesoscale model (MM5; Grell et al., 1994). Sparse Matrix Operator Kernel 107 Emission (SMOKE; Houyoux et al. 2000) gridded hourly emissions were built from USEPA's 108 2002 national emission inventory (NEI) v3 with year-specific adjustments for emissions from 109 110 major point sources, mobile sources, and fires. Details of the meteorological modeling, emissions processing, CMAQ inputs and CMAQ model configuration can be found in Appel et al. (2011). 111 CMAQ-modeled species included reduced N: ammonia (NH₃) and ammonium (NH₄⁺), and 112 oxidized N: nitrogen oxide (NO), nitrogen dioxide (NO₂), nitrate (NO₃), nitrous acid (HNO₂), 113 114 nitric acid (HNO₃), dinitrogen pentoxide (N₂O₅), nitrate (NO₃), organic nitrate, peroxyacetyl 115 nitrate (PAN) and higher PANs. 116 117 Additional files representing 2020 projected emissions based on expected growth and emission reductions due to the Clean Air Interstate Rule (CAIR, replaced with Cross-State Air Pollution 118 119 Rule), Tier 2 Vehicle and Gasoline Sulfur Rule, Heavy Duty Highway Rule, and Non-Road 120 Diesel Rule (Houyoux, 2005; USEPA, 2011a; USEPA, 2011b) were used to evaluate the effects 121 on N deposition of proposed air quality regulations. These 2020 CMAQ files were made available by the USEPA and were based on the same MM5 meteorology as the 2002 CMAQ 122 123 runs from Appel et al. (2011) with only the emissions inventory changed.

94

96

97

99

100

101

125	The Watershed Deposition Tool (WDT)
126	
127	USEPA has developed the WDT to facilitate the extraction and analysis of CMAQ gridded
128	output data for irregular spatial delineations such as basins and watersheds (Schwede et al.,
129	2009). We downloaded the WDT (USEPA, 2011c) and available CMAQ v4.7 output files
130	(USEPA, 2011d). Watershed basin polygons obtained from the Tampa Bay Estuary Program's
131	(TBEP's) on-line technical resources were modified to better define water and land polygons and
132	to achieve a finer spatial resolution (TBEP, 2011). In WDT, CMAQ's grid cells were
133	superimposed over the watershed basins and bay segments as shown in Figure 3. WDT
134	calculates N deposition for each watershed basin or bay segment as the summed product of
135	deposition for each grid cell and the fraction of the overlay area between grid cell and polygon.
136	Average N deposition rates are calculated as basin or bay segment N deposition divided by its
137	area (Widing, 2006).
138	
139	N Loading Estimates
140	
141	For direct N loading to Tampa Bay, we integrated the bay segment-specific loading rates; for
142	indirect N loading, we integrated basin-specific rates and assumed that $18\ \%$ of atmospherically-
143	deposited N was transferred from land to bay (Pollman and Poor, 2003). Atmospheric loading
144	rates were calculated separately for dry- and wet-deposited N and for oxidized and reduced N.
145	
146	Modeled versus Measured Wet Deposition
147	
148	Long-term monthly rainfall amount and N concentration data were available for Verna
149	Wellfield (FL 41), a NADP National Trends Network (NTN) site (NADP, 2011), which is
150	located in Sarasota County and is proximate to the southern boundary of Tampa Bay's watershed
151	(Figure 1). From the Verna Wellfield data, wet deposition rates were calculated according to eq
152	1, where C is the monthly volume-weighted rainfall concentration of either NO_3^- -N or NH_4^+ -N
153	and has units of mg l^{-1} , D is the rainfall depth and has units of cm mo ⁻¹ , and F is the deposition
154	rate (i. e., flux) and has units of kg N ha ⁻¹ mo ⁻¹ . Concentration and precipitation data for August
155	2005 were not available in the downloaded file.

$$F = 0.100 \cdot C \cdot D \tag{1}$$

From the simulations of Appel et al. (2011), we obtained CMAQ-modeled precipitation amount and HNO₃, NO₃⁻, NH₃, and NH₄⁺ wet N deposition rates, as well as oxidized N and reduced N wet deposition rates for the 12-km x 12-km grid cell that enclosed NADP's Verna Wellfield (FL 41) site. CMAQ-modeled oxidized N deposition rates for Verna Wellfield were ~99% aerosol NO₃⁻ with minor contributions from NO_x, HNO₃, organic N, PAN, and other oxidized N species. For this reason we have labeled our graphics and tables as NO₃⁻-N rather than oxidized N wet deposition rates. CMAQ-modeled reduced N deposition rates for Verna Wellfield were ~100% aerosol NH₄⁺ with minor contributions from NH₃.

Pearson correlation coefficient (r), normalized mean bias (NMB, eq 2), normalized mean error (NME, eq 3), and root mean squared error (RMSE, eq 4) were computed and plots prepared to assess agreement between modeled and observed wet N deposition rates (Nolte et al., 2008).

$$NMB = 100 \% \cdot \Sigma \left(C_{\text{mod}} - C_{\text{obs}} \right) / \Sigma C_{\text{obs}}$$
 (2)

$$NME = 100 \% \cdot \Sigma |C_{\text{mod}} - C_{\text{obs}}| / \Sigma C_{\text{obs}}$$
(3)

176
$$RMSE = \sqrt{(1/n)} \cdot \sum (C_{\text{mod}} - C_{\text{obs}})^2$$
, where *n* is the number of observations (4)

RESULTS AND DISCUSSION

N Loading to Tampa Bay and Its Watershed

The CMAQ model yielded loading rates of 1,080 metric tons N yr⁻¹ to Tampa Bay and 8,280 metric tons N yr⁻¹ to the land portion of its watershed. If we assume a watershed-to-bay transfer rate of 18 % (Poor and Pollman, 2003), atmospheric direct and indirect loading rates to Tampa Bay were 1,080 metric tons N yr⁻¹ and 1,490 metric tons N yr⁻¹, respectively, or an atmospheric

187 segment. 188 189 Poe et al. (2005) estimated direct atmospheric and total loading rates for 2002 to Tampa Bay of 190 840 metric tons N and 3,400 metric tons N, respectively. To determine the relative fraction of 191 CMAQ-modeled atmospheric loading to total loading, we first adjusted the 2002 total N loading rate from Poe et al. (2005) for the CMAQ-modeled direct atmospheric N loading rate (3,400 -192 840 + 1,080 = 3,640 metric tons) and second computed the fraction of atmospheric to total 193 loading rates (2,570 metric tons N/3,640 metric tons N), which was 71 % and a significant 194 fraction of Tampa Bay's total N loading rate. JEI (2008) estimated direct atmospheric and total N 195 loading rates to Tampa Bay for 2003 through 2006 (Table 2). Using the approach just described, 196 we calculated from the CMAQ-model output the direct and indirect atmospheric N loading and 197 fraction of total N loading that is atmospheric for 2003 through 2006 (Table 2). Atmospheric 198 loading rates ranged from 1,950 to 2,260 metric tons N yr⁻¹, with significant fractional 199 contributions that ranged from 35 % to 63 %. Contemporary published values for atmospheric 200 loading rates to Tampa Bay vary from 1,100 metric tons N yr⁻¹ to 3,030 metric tons N yr⁻¹. The 201 broad range in estimates suggests significant differences in measurement techniques, 202 computational tools, and methodical assumptions (Poor et al., in preparation). 203 204 The WDT's graphical results for atmospheric N deposition rates are shown Figures 3, 4, and 5. 205 For 2002, the CMAQ-modeled average atmospheric deposition rate across the bay and its 206 watershed was 13.3 kg N ha⁻¹ yr⁻¹. Based on the 12-km x 12-km grid cell size, deposition rates 207 ranged from 6.24 kg N ha⁻¹ yr⁻¹ to 21.4 kg N ha⁻¹ yr⁻¹, with the lowest rates predicted over the 208 Gulf of Mexico and highest rates centered on Tampa's urban core, which reflected emissions 209 from the underlying human settlements (Figure 3). These N deposition rates are characteristic of 210 an estuary and watershed with moderate N pollution (Dentener et al., 2006; Holland et al., 2005). 211 212 For dry- and wet-deposited N, the 2002 modeled average atmospheric deposition rates were 213 7.70 kg N ha⁻¹ yr⁻¹ and 5.64 kg N ha⁻¹ yr⁻¹, respectively (Figure 4). Over land, the dry and wet 214 loading rates were 4,800 metric tons N yr⁻¹ and 3,490 metric tons N yr⁻¹, respectively; over 215 water, the dry and wet loading rates were 608 metric tons N yr⁻¹ and 474 metric tons N yr⁻¹, 216

loading rate to the bay of 2,570 metric tons N yr⁻¹. Table 1 shows N loading rates by bay

respectively. Assuming an 18 % transfer rate of N from land to water, atmospheric loading rates to Tampa Bay were 57 % dry and 43 % wet N deposition. Dry N deposition rates were higher in sectors with major traffic corridors and power generation plants near Tampa Bay. Modeled spatial gradients of wet N deposition were flatter than corresponding dry deposition N gradients (Figure 4).

For oxidized and reduced N, the 2002 modeled average atmospheric deposition rates were 9.73 kg N ha⁻¹ yr⁻¹ and 3.61 kg N ha⁻¹ yr⁻¹, respectively (Figure 5). Over land, the oxidized and reduced loading rates were 5,990 metric tons N yr⁻¹ and 2,300 metric tons N yr⁻¹, respectively; over water, the oxidized and reduced loading rates were 842 metric tons N yr⁻¹ and 240 metric tons N yr⁻¹, respectively. Assuming an 18 % transfer rate of N from land to water, atmospheric loading rates to Tampa Bay were 75 % oxidized N and 25 % reduced N. The distribution of reduced N deposition was higher east of the bay over a region of industrial NH₃ emissions, a trend also seen for wet N deposition (Figure 4).

CMAQ-Modeled Temporal Trends in N Deposition

Between 2005 and 2010, Florida's annual and ozone season oxidized N emissions from power plants had dropped by 0.11 million metric tons (63%) and 0.054 million metric tons (65%), respectively (USEPA, 2011b), and continued a decade-long downward trend in both power plant NO_x emissions and NO_x concentrations measured at urban monitors near Tampa Bay (Poor et al., in preparation). The observed downward trend in atmospheric NO_x concentrations may have important consequences for N deposition to Tampa Bay. According to CMAQ modeling results, dry N deposition dominates both spatial and temporal N deposition rates within Tampa Bay and its watershed. These results suggest that within a watershed monitoring dry N deposition may be as important as monitoring wet N deposition.

By comparison, between 2002 and 2006 the CMAQ-modeled annual average N deposition rates to Tampa Bay and its watershed suggested a modest decline of 3.1 kg N ha⁻¹ yr⁻¹. Of this decline, 0.66 kg N ha⁻¹ yr⁻¹ was from dry deposition of oxidized N, 0.70 kg N ha⁻¹ yr⁻¹ from wet deposition of reduced N, and 1.77 kg N ha⁻¹ yr⁻¹ from wet deposition of oxidized N; dry

deposition of reduced N increased by $0.03 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Figure 6). We investigated whether a decline in wet N deposition could be discerned at Verna Wellfield (FL 41), which is the NADP site nearest to Tampa Bay's watershed (Figure 1). We applied an unpaired, two-sided Student's t-test to test the hypothesis that between the first 30 months and the second 30 months of the 5-yr period the means of log-transformed NO₃-N or NH₄⁺-N deposition rates were equal. This hypothesis was not rejected for either NO₃-N or NH₄⁺-N deposition rates (p = 0.67 and p = 0.17, respectively). Our approach was repeated for rainfall rates and for NO₃ or NH₄⁺ concentrations with similar results. Thus, no significant downward trend in N wet deposition was evident at Verna Wellfield. Small changes in N deposition are likely difficult to discern over short time periods and among the large swings in rainfall and wet deposition rates (Figure 7).

In Figure 7 we illustrate for Tampa Bay and its watershed the temporal variation in modeled monthly dry and wet N deposition rates, which for the 5-year period shown, had means (± standard deviation) of 0.605 (± 0.081) and 0.365 (± 0.340), respectively. Given their relatively low coefficient of variation (CV), dry N deposition rates were well-predicted by an average value. This was clearly not the case for wet N deposition rates, as temporal gradients were steep with the highest rates seen in mid-summer. Dry-to-wet N deposition ratios were 5.99 (± 5.17) when averaged over the drier months September through May, and 0.801 (± 0.172) when averaged over the wetter months June through July. Annual watershed dry-to-wet N deposition ratios varied from 3.03 in 2002 to 6.48 in 2006 (a dry year) if calculated as the average of monthly dry-to-wet ratios, and from 1.36 in 2002 to 2.22 in 2006 if calculated as the average of annual dry deposition to wet deposition. One can see the challenges in using dry-to-wet N deposition ratios to predict from wet N deposition the dry N deposition to the watershed.

Comparison of Modeled and Observed Wet N Deposition Rates

Long-term wet deposition monitoring at an NADP NTN station proximate to the southern end of Tampa Bay's watershed offered us an opportunity to assess the agreement between CMAQ modeling and observations of rainfall and wet N deposition rates. This comparison was of a predicted grid cell average and a point measurement of rainfall amount or N deposition rate, which is by itself a source of error (Davis and Swall, 2006).

279 Gases of HNO₃, HONO, and NH₃ are water soluble and are thus scavenged by rainfall. 280 281 Precipitation acidity in the range of pH 4-5 (Strayer et al., 2007) favors the disassociation of these compounds into NO₃, NO₂, and NH₄ in rainfall samples. Water-dissolved NO₂ slowly 282 oxidizes to NO₃ (Finlayson-Pitts and Pitts, 2000) during the collection, transport, and storage of 283 rainfall samples prior to their analysis at NADP's central laboratory. Aerosols containing NO₃ 284 and NH₄⁺ are also removed by rainfall, albeit with differing size-related removal efficiencies 285 (Finlayson-Pitts and Pitts, 2000). Gases of NO and NO₂ are poorly water soluble but may 286 interact with an aerosol surface to form HONO; N₂O₅ readily dissolves in water to form NO₃ 287 and NO₂ (Finlayson-Pitts and Pitts, 2000). Thus, NADP-reported concentrations of NO₃ and 288 NH₄⁺ include both gas and particle contributions. 289 290 291 In CMAO-modeled wet N deposition, error is present in the emissions inventory, meteorology, and mechanistic representations of atmospheric chemistry and physics. Such errors are discussed 292 by Gilliland et al. (2006), who proposed corrections to the NEI for seasonality of NH₃ emissions; 293 by Davis and Swall (2006), based on their examination of the effect of MM5's simulation of 294 precipitation on CMAO-modeled NH₄⁺ wet deposition; and by Chemel et al. (2011) from their 295 296 investigation of CMAQ's ability to predict a power plant's contribution to N deposition, as 297 examples. 298 299 Error is present both in CMAQ-modeled and observed wet N deposition rates, so care must be taken not to assign all of the disagreement to modeling. According to Wetherbee et al. (2006), 300 for example, "atmospheric wet deposition is slightly underestimated in 48 to 68 percent of the 301 NADP/NTN samples, depending on the analyte." This underestimate is a consequence of analyte 302 303 loss during field exposure, sampling handling, and/or shipping. Atmospheric wet deposition is overestimated if the sample is marginally contaminated; gross contamination, however, leads to 304 sample rejection and loss of data, which if uncorrected, causes an underestimate in cumulative 305 306 atmospheric wet deposition.

For eastern US, MM5 -simulated precipitation rates were underestimated for synoptic-scale storm systems and overestimated for sub-grid scale convective storm systems (Appel et al.,

307

308

2011; Davis and Swall, 2006). A similar trend is evident at NADP's Verna Wellfield (FL 41) site, where reasonable agreement was seen between modeled and observed rainfall rates for cooler and drier months when rainfall was more likely produced by a synoptic system but a moderate positive bias was seen for summertime (wetter) months when rainfall was more likely generated in convective storms (Figure 8). Over a 5-yr period, the modeled and measured precipitation rates were moderately correlated, with averages of 16.3 cm and 12.3 cm, respectively (Table 3); 62 % of the modeled monthly rainfall rates were within a factor of two of observed rainfall rates (Figure 8). Since deposition rates are the product of N concentration and rainfall rate (eq 1), a bias in rainfall rate will contribute to a bias in N wet deposition.

The CMAQ model predictions of wet deposition rates agreed remarkably well for NO₃⁻-N and NH₄⁺-N, with a only small positive bias relative to observations (Table 3) as shown in Figures 9 and 10; 75 % and 54 % of the data points for wet deposition rates of NO₃⁻-N and NH₄⁺-N were within a factor of two, respectively (Figures 9 and 10). The N wet deposition biases were not as large as the precipitation bias, which suggested that errors in precipitation rates were offset by errors in N concentrations; in other words, NO₃⁻ and NH₄⁺ concentrations were biased low. Appel et al. (2011) found that for eastern US, CMAQ-modeled wet deposition of both NO₃⁻-N and NH₄⁺ -N were underestimated but that these biases were diminished when model simulations were corrected for lightning-generated NO and bi-directional NH₃ exchange. The better model performance for NO₃⁻-N relative to NH₄⁺-N wet deposition reflects, perhaps, differences in spatial and temporal resolution of NO_x and NH₃ emissions inventories (Appel et al., 2011; Gilliland et al., 2006) and the lower uncertainty in the NOx emissions compared to NH₃ emissions.

2002 and 2020 N Emission Scenarios

Through the Clean Air Interstate Rule (CAIR, replaced with Cross-State Air Pollution Rule), Tier 2 Vehicle and Gasoline Sulfur Rule, Heavy Duty Highway Rule, and Non-Road Diesel Rule (USEPA, 2011c, d), USEPA seeks to improve air quality by phased reductions in air pollutant emissions from both fixed and mobile sources. A fully implemented CAIR, for example, removes 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). By 2020, NH₃ emissions are expected to grow by 0.44 million metric tons for all states in the continental US, however, of which 0.22 million metric tons of NH₃ emissions are from states in the eastern US (Houyoux, 2005). Moreover, slated reductions in sulfur dioxide (SO₂) emissions will shift aerosol NH₄⁺ to gaseous NH₃ and thus favor localized dry deposition of reduced N (Pinder et al., 2008).

For 2002, the CMAQ-modeled direct plus indirect atmospheric loading rate to Tampa Bay was 2,570 metric tons N. Using WDT, we calculated the potential impact of fully implemented CAIR (now Cross-State Air Pollution Rule), Tier 2 Vehicle and Gasoline Sulfur Rules, Heavy Duty Highway Rule, and Non-Road Diesel Rule. Between the 2002 and 2020 emission scenarios, the projected change in atmospheric N loading was 857 metric tons N, which represented 33 % less atmospheric N loading and 24 % less total N loading to Tampa Bay.

Changes in atmospheric N deposition rates across Tampa Bay and its watershed between the 2002 and 2020 emissions scenarios are shown in Figure 11 and revealed a broad decrease of 1 to 2 kg N ha⁻¹ over the entire watershed (orange color in Figure 11 A) but as high as 6 to 7 kg N ha⁻¹ in the vicinity of major power plant and industrial sources (gray color in Figure 11 A). Thus, both regional and local emissions controls explain reductions in atmospheric N deposition under the future emissions scenario.

CONCLUSIONS

The Water Deposition Tool (WDT) offers a user-friendly interface with CMAQ model output to calculate atmospheric deposition of N to watersheds and their basins. Output made available includes wet and dry reduced N deposition and wet and dry oxidized N deposition on a 12-km x 12-km grid scale. With WDT we were able to estimate N deposition to both land and bay portions of the watershed and thereby include direct and indirect atmospheric deposition components. Modeled atmospheric N loading represented a substantial fraction of the total N loading to Tampa Bay. WDT also opened the door for trend analysis of CMAQ model output. As examples, CMAQ modeling indicated that during an extended dry season, dry N deposition dominated N deposition rates to Tampa Bay and its watershed. Moreover, oxidized N deposition

rates greatly exceeded reduced N deposition rates. With WDT we had the opportunity to 372 373 compare past and future emissions scenarios to assess the impact of emissions controls on N deposition to Tampa Bay and its watershed. Simulations of a fully-implemented CAIR (now 374 Cross-State Air Pollution Rule) along with transportation-related rules translated into a 375 376 significant reduction in total N loading to Tampa Bay. 377 ACKNOWLEDGMENTS 378 379 This research was funded by Florida Department of Environmental Protection (FDEP) through 380 Tampa Bay Estuary Program (TBEP) under FDEP Contract AQ206. Noreen Poor is affiliated 381 with the University of South Florida College of Public Health. The United States Environmental 382 Protection Agency through its Office of Research and Development collaborated in the research 383 described here. It has been subjected to Agency review and approved for publication. 384 385 386 REFERENCES 387 Appel, K.W., K.M. Foley, J.O. Bash, R.W. Pinder, R.L. Dennis, D.J. Allen, and K. Pickering. 388 389 2011. A multi-resolution assessment of the Community Multiscale Air Quality (CMAQ) model v4.7 wet deposition estimates for 2002-2006. Geoscientific Model Development 4: 357-371. 390 391 Byun, D. and K.L. Schere. 2006. Review of governing equations, computational algorithms, and 392 other components of the Models-3 Community Multiscale Air Quality (CMAQ) Modeling 393 394 System. Applied Mechanics Reviews 59: 51-77. 395 396 Carstensen, J., M. Sánchez-Camacho, C.M. Duarte, D. Krause-Jensen, and N. Marbà. 2011. Connecting the dots: Responses of coastal ecosystems to changing nutrient concentrations. 397 Environmental Science and Technology dx.doi.org/10.1021/es202351y. 398 399 Chemel, C., R.S. Sokhi, A.J. Dore, P. Sutton, K.J. Vincent, S.J. Griffiths, G.D. Hayman, R.D. 400 Wright, M. Baggaley, S. Hallsworth, H.D. Prain, and B.E.A. Fisher., 2011. Predictions of U. K. 401

- 402 regulated power station contributions to regional air pollution and deposition: A model
- 403 comparison exercise. Journal of the Air & Waste Management Association 61: 1236-1245.

- 405 Conley, D.J., H.W. Paerl, R.W. Howarth, D.F. Boesch, S.P. Seitzinger, K.E. Havens, C.
- 406 Lancelot, and G. Likens. 2009. Controlling eutrophication: nitrogen and phosphorus. Science
- 407 323: 1014-1015.

408

- Davis, J.M., and J.L. Swall. 2006. An examination of the CMAQ simulations of the wet
- deposition of ammonium from a Bayesian perspective. *Atmospheric Environment* 40: 4562-4573.

411

- Dennis, R.L., and J.R. Arnold. 2007. CMAQ-UCD Atmospheric Deposition Estimates to Tampa
- 413 Bay Watershed Sub-basins and Tampa Bay Waters. Prepared for Tampa Bay Estuary Program,
- 414 St. Petersburg, Florida.

415

- 416 Dentener, F., et al. 2006. Nitrogen and sulfur deposition on regional and global scales: A
- 417 multimodel evaluation. Global Biogeochemical Cycles 20: GB4003,
- 418 doi:10.1029/2005GB002672.

419

- 420 Dixon, L.K., G.A. Vargo, J.O.R. Johansson, R.T. Montgomery, M.B. Neely. 2009. Trends and
- 421 explanatory variables for the major phytoplankton groups of two southwestern Florida estuaries,
- 422 U. S. A. Journal of Sea Research 61: 95-102.

423

- 424 Finlayson-Pitts, B. J., and J. N. Pitts, Jr. 2000. Chemistry of the Upper and Lower Atmosphere,
- 425 San Diego, California: Academic Press.

426

- 427 Gilliland, A.B., K.W. Appel, R.W. Pinder, and R.L. Dennis. 2006. Seasonal NH₃ emissions for
- 428 the continental United States: Inverse model estimation and evaluation. Atmospheric
- 429 Environment 40: 4986-4998.

- 431 Greening, H.S., L.M. Cross, and E.T. Sherwood. 2011. A multiscale approach to seagrass recovery in
- 432 Tampa Bay, Florida. Ecological Restoration 29: 82-93.

- 434 Greening, H., and A. Janicki. 2006. Toward reversal of eutrophic conditions in a subtropical
- 435 estuary: water quality and seagrass response to nitrogen loading reductions in Tampa Bay,
- 436 Florida, USA. Environmental Management 38:163-178.

437

- 438 Grell, G.A., J. Dudhia, and D.R. Stauffer. 1994. A Description of the Fifth Generation Penn
- 439 State/NCAR Mesoscale Model (MM5). NCAR Tech Note, NCAR/TN-398+STR, Boulder,
- 440 Colorado, 138 pp.

441

- Holland, E.A., B.H. Braswell, J. Sulzman, and J.-F. Lamarque. 2005. Nitrogen deposition onto
- 443 the United States and Western Europe: Synthesis of observations and models. Ecological
- 444 Applications 15: 38-57.

445

- Houyoux, M.R., J.M. Vukovich, C.J. Coats, Jr., N.J.M. Wheeler, and P.S. Kasibhatla. 2000.
- 447 Emission inventory development and processing for the seasonal model or regional air quality
- 448 (SMRAQ) project, Journal of Geophysical Research, Atmospheres, 105:D7, 9079-9090.

449

- 450 Houyoux, M. 2005. Clear Air Interstate Rule: Emissions Inventory Technical Support
- 451 Document, United States Environmental Protection Agency. Available for download at
- 452 http://www.epa.gov/cair/technical.html.

453

- Howarth, R.W., and R. Marino. 2006. Nitrogen as the limiting nutrient for eutrophication in
- coastal marine ecosystems evolving views over three decades. Limnology and Oceanography 51:
- 456 364-376.

457

- 458 Janicki, A., and D. Wade. 1996. Estimating Critical External Nitrogen Loads for the Tampa Bay
- 459 Estuary: An Empirically Based Approach to Setting Management Targets. St. Petersburg, FL:
- 460 Tampa Bay National Estuary Program

- Janicki Environmental, Inc. (JEI). 2008. Estimates of Total Nitrogen, Total Phosphorus, Total
- 463 Suspended Solids, and Biochemical Oxygen Demand Loadings to Tampa Bay, Florida: 2004-
- 464 2007. Tallahassee, FL: Florida Department of Environmental Protection.

- Johannson, J.O.R., 2009. Nutrient Enrichment Studies of Natural Phytoplankton Populations in
- Tampa Bay: A Summary of Results June 1993 to August 2009. Tampa, FL: City of Tampa
- 468 Wastewater Department Bay Study Group.

469

- 470 NADP, 2011. National Atmospheric Deposition Program, National Trends Network,
- http://nadp.sws.uiuc.edu/ntn/ (accessed November 2, 2011).

472

- Nolte, C.G., P.V. Bhave, J.R. Arnold, R.L. Dennis, K.M. Zhang, and A.S. Wexler. 2008.
- 474 Modeling urban and regional aerosols—Application of the CMAQ-UCD aerosol module to
- 475 Tampa, a coastal urban site. Atmospheric Environment 42: 3179-3191.

476

- 477 Pinder, R.W., A.B. Gilliland, and R.L. Dennis. 2008. Environmental impact of atmospheric NH₃
- 478 emissions under present and future conditions in eastern United States. Geophysical Research
- 479 Letters 35: L12808, doi: 10.1029/2008GL033732.

480

- 481 Poe, A., K. Hackett, S. Janicki, R. Pribble, and A. Janicki. 2005. Estimates of Total Nitrogen,
- 482 Total Phosphorus, Total Suspended Solids, and Biochemical Oxygen Demand Loadings to
- 483 Tampa Bay, Florida: 1999-2003, Final Report, March 2005. Tampa Bay Estuary Program
- 484 Technical Publication #02-05, St. Petersburg, FL, pp. 374.

485

- 486 Pollman, C., and N.D. Poor. 2003. Export of Atmospherically Derived Nitrogen in the Tampa
- 487 Bay Watershed. Presented at American Geophysical Union (AGU) Fall Meeting, San Francisco,
- 488 CA, 8-12 December.

- 490 Poor, N. 2008. Nitrogen Emission/Deposition Ratios for Air Pollution Sources that Contribute to
- 491 the Nitrogen Loading of Tampa Bay. Tampa, FL: Environmental Protection Commission of
- 492 Hillsborough County.

493	
494	Poor, N., Cross, L, Dennis, R. L. Synthesis of Bay Region Atmospheric Chemistry Experiment
495	(BRACE) and implications for nitrogen management of Tampa Bay. In preparation.
496	
497	Poor, N., C. Pollman, P. Tate, M. Begum, M. Evans, and S. Campbell. 2006. Nature and
498	magnitude of atmospheric fluxes of total inorganic nitrogen and other inorganic species to the
499	Tampa Bay Watershed, FL, USA. Water, Air, and Soil Pollution 170: 267-283.
500	
501	Poor, N., R. Pribble, and H. Greening. 2001. Direct wet and dry deposition of ammonia, nitric
502	acid, ammonium, and nitrate to the Tampa Bay Estuary, FL, USA. Atmospheric Environment 35:
503	3947-3955.
504	
505	Pribble, R., A. Janicki, H. Zarbock, S. Janicki, and M. Winowitch. 2001. Estimates of Total
506	Nitrogen, Total Phosphorus, Total Suspended Solids, and Biochemical Oxygen Demand
507	Loadings to Tampa Bay, Florida: 1995-1998, Final Report, July 2001. St. Petersburg, FL: Tampa
508	Bay Estuary Program.
509	
510	Schwede, D.B., R.L. Dennis, and M.A. Bitz. 2009. The Watershed Deposition Tool (WDT): A
511	tool for incorporating atmospheric deposition in water-quality analyses. Journal of the American
512	Water Resources Association 45: 973-985.
513	
514	Smith, V. 2006. Responses of estuarine and coastal marine phytoplankton to nitrogen and
515	phosphorus enrichment. Limnology and Oceanography 51: 377-384.
516	
517	Tampa Bay Estuary Program (TBEP), 2011. www.tbeptech.org: TBEP Tech Resources,
518	Available Databases, TBEP GIS Resources, Major Drainage Basins Delineated in Tampa Bay,
519	(accessed October 18, 2011).
520	
521	Tampa Bay Nitrogen Management Consortium (TBNMC), 2010. 2009 Reasonable Assurance
522	Addendum: Allocation and Assessment Report. Tampa Bay Estuary Program Technical

Publication #03-10. St. Petersburg, FL: Tampa Bay Estuary Program.

524	
525	Wang, P.F., J. Martin, and G. Morrison. 1999. Water quality and eutrophication in Tampa Bay,
526	Florida. Estuarine, Coastal and Shelf Science 49: 1-20.
527	
528	USEPA, 2011a. Clear Air Interstate Rule, www.epa.gov/cair/. United States Environmental
529	Protection Agency (accessed October 26, 2011).
530	
531	USEPA, 2011b. Cross-State Air Pollution Rule, www.epa.gov/airtransport/. United States
532	Environmental Protection Agency (accessed October 26, 2011).
533	
534	USEPA, 2011c. Watershed Deposition Tool,
535	http://www.epa.gov/AMD/EcoExposure/depositionMapping.html. United States Environmental
536	Protection Agency(accessed October 17, 2011).
537	
538	USEPA, 2011d. Watershed Deposition Tool Data,
539	http://www.epa.gov/AMD/EcoExposure/WDTData.html. United States Environmental Protection
540	Agency (accessed October 17, 2011).
541	
542	Wetherbee, G. A., N.E. Latysh, and S.M. Greene. 2006. External Quality-Assurance Results for
543	the National Atmospheric Deposition Program/National Trends Network and Mercury
544	Deposition Network, 2004. Scientific Investigations Report 2006-5067. Reston, Virginia: U. S.
545	Geological Survey.
546	
547	Widing, M.A. 2006. Watershed Deposition Tool (WDT): User's Manual. Prepared for USEPA.
548	http://www.epa.gov/AMD/EcoExposure/depositionMapping.html, accessed October 17, 2011.
549	
550	
551	
552	
553	
554	

TABLES

Table 1. Estimated 2002 direct and indirect atmospheric N loading rates within Tampa Bay's watershed. Water area includes embayment, canals, and major tributaries apportioned by bay segment; land area includes watershed drainage surface by bay segment.

Bay Segment	Water Area, ha	Land Area, ha	Direct Atmospheric Loading, metric tons N	*Indirect Atmospheric Loading, metric tons N	Atmospheric Loading, metric tons N	
Old Tampa	22,451	67,326	261	181	441	
Hillsborough	10,852	330,364	211	843	1050	
Middle Tampa	29,450	79,924	286	194	480	
Lower Tampa	25,265	8,437	218	19.2	237	
Boca Ciega	6,188	21,353	43.6	52.5	96.1	
Terra Ceia	1,650	2,851	20.6	6.48	27.1	
Manatee River	3,460	92,416	42.1	196	238	
Totals	99,317	602,669	1,080	1,490	2,570	

^{*}Assumes an 18 % transfer rate from watershed to bay.

Table 2. Modeled atmospheric deposition (AD) and total N loading to Tampa Bay 2002-2006.

	Prev	vious Estima	ites*		Current I	Estimates	
Year	N Loading, metric tons	Total N Loading, metric tons	§Adjusted Total N Loading, metric tons	N Loading, metric tons	Indirect AD N Loading, metric tons	AD N Loading, metric tons	Total N Loading that is AD Loading, %
2002	840	3,400	3,640	1,080	1,490	2,570	70.6
2003	1,150	6,690	6,440	903	1,340	2,240	34.8
2004	801	5,930	6,010	885	1,240	2,120	35.4
2005	603	3,230	3,570	950	1,310	2,260	63.3
2006	552	2,980	3,230	803	1,150	1,950	60.5

*JEI, 2008; TBNMC, 2010; \$Previous estimate of total N loading – previous estimate of direct

AD N loading + current estimate of direct AD N loading

Table 3. Statistics to assess agreement between modeled vs. observed monthly rainfall and wet N deposition rates. Units are cm on mean modeled, mean observed, and RMSE precipitation; units are kg ha⁻¹ mo⁻¹ on mean modeled, mean observed, and RMSE N deposition rates.

Species	Mean Modeled	Mean Observed	r, %	NMB, %	NME, %	RMSE
Precipitation	16.3	12.3	73.7	32.6	66.8	12.6
NH_4^+ -N	0.113	0.108	50.1	2.91	62.1	0.103
NO_3 -N	0.173	0.166	78.6	0.416	43.4	0.107
Total N	0.287	0.274	73.7	1.39	43.3	0.186

584	
585	FIGURE TITLES
586	
587	Figure 1. Tampa Bay and its watershed. Black outlines indicate watershed basin and bay
588	segments boundaries and darker shading shows municipal boundaries for major cities.
589	
590	Figure 2. Watershed Deposition Tool (WDT) display for total annual N deposition by basins and
591	bay segments within Tampa Bay's watershed for 2002.
592	
593	Figure 3. Reactive nitrogen (N) atmospheric deposition rates for Tampa Bay and its watershed
594	from 2002 CMAQ model simulations. A: gridded N deposition rates (kg N ha ⁻¹); B: average N
595	deposition rates by watershed basin and bay segment (kg N ha-1).
596	
597	Figure 4. Atmospheric average dry (A) and wet (B) N deposition rates for Tampa Bay and its
598	watershed, by watershed basin and bay segment (kg N ha-1), from 2002 CMAQ model
599	simulations.
600	
601	Figure 5. Atmospheric average oxidized (A) and reduced (B) N deposition rates for Tampa Bay
602	and its watershed, by watershed basin and bay segment (kg N ha-1), from 2002 CMAQ model
603	simulations. White indicates deposition rates < 2 kg N ha ⁻¹ .
604	
605	Figure 6. Modeled average wet and dry N deposition rates for Tampa Bay and its watershed.
606	
607	Figure 7. CMAQ-predicted 2002-2006 annual average N deposition rates for Tampa Bay and its
608	watershed.
609	
610	Figure 8. Comparison of CMAQ-modeled and observed precipitation rates for NADP's Verna
611	Wellfield (FL41) site.
612	
613	Figure 9. Comparison of CMAQ-modeled and observed NO ₃ wet deposition rates for NADP's
614	Verna Wellfield (FL41) site.

Figure 10. Comparison of CMAQ-modeled and observed NH₄⁺ wet deposition rates for NADP's Verna Wellfield (FL41) site. Figure 11. CMAQ-modeled changes in watershed N deposition for 2002 base case and 2020 future scenario emissions for Tampa Bay and its watershed, processed with WDT from CMAQ 2002 12-km gridded scale output. A: change in gridded N deposition rates (kg-N ha⁻¹); B: change in average N deposition rates by watershed basin and bay segment (kg-N ha⁻¹).

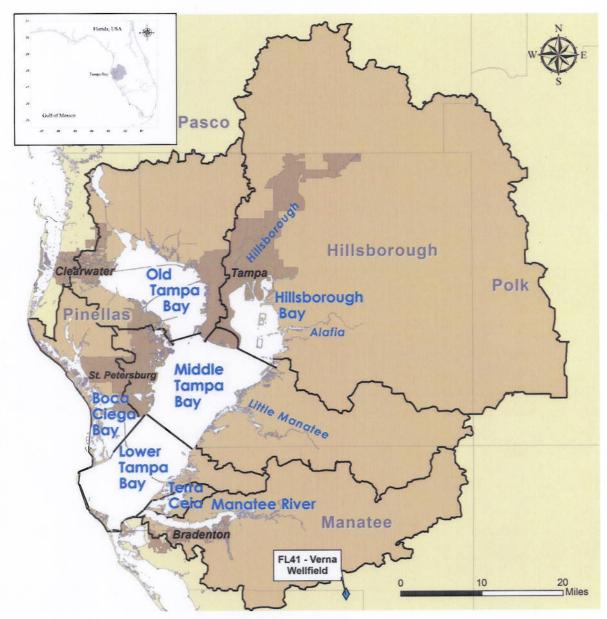


Figure 1. Tampa Bay and its watershed. Black outlines indicate watershed basin and bay segments boundaries and darker shading shows municipal boundaries for major cities.

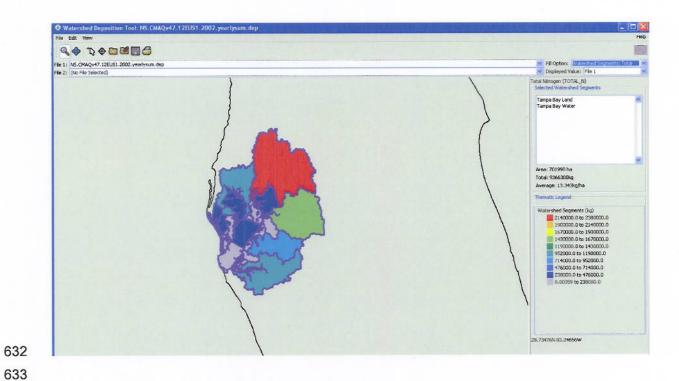


Figure 2. Watershed Deposition Tool (WDT) display for total annual N deposition by basins and bay segments within Tampa Bay's watershed for 2002.

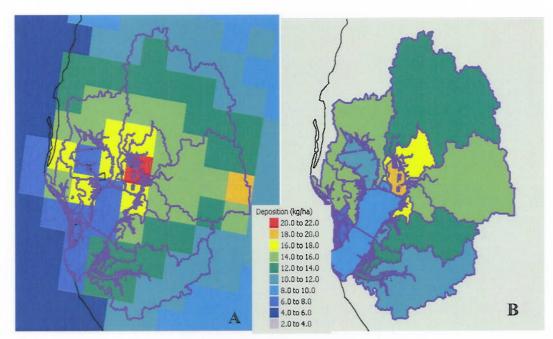


Figure 3. Reactive nitrogen (N) atmospheric deposition rates for Tampa Bay and its watershed from 2002 CMAQ model simulations. A: gridded N deposition rates (kg N ha⁻¹); B: average N deposition rates by watershed basin and bay segment (kg N ha⁻¹).

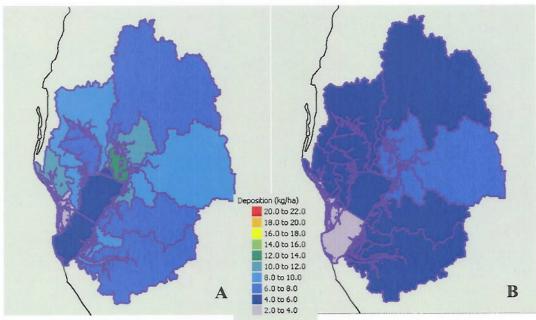


Figure 4. Atmospheric average dry (A) and wet (B) N deposition rates for Tampa Bay and its watershed, by watershed basin and bay segment (kg N ha⁻¹), from 2002 CMAQ model simulations.



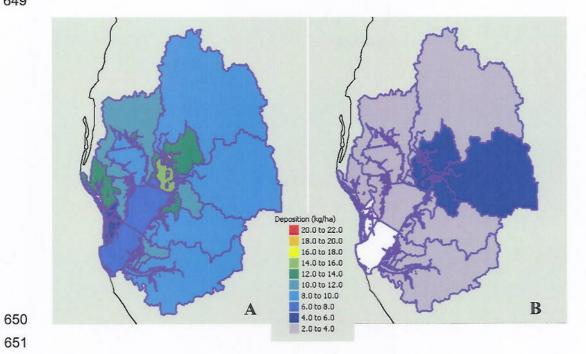


Figure 5. Atmospheric average oxidized (A) and reduced (B) N deposition rates for Tampa Bay and its watershed, by watershed basin and bay segment (kg N ha⁻¹), from 2002 CMAQ model simulations. White indicates deposition rates < 2 kg N ha⁻¹.

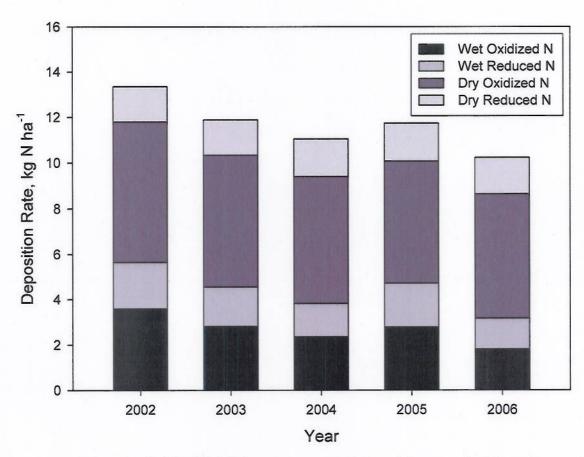


Figure 6. CMAQ-modeled 2002-2006 annual average N deposition rates for Tampa Bay and its watershed.

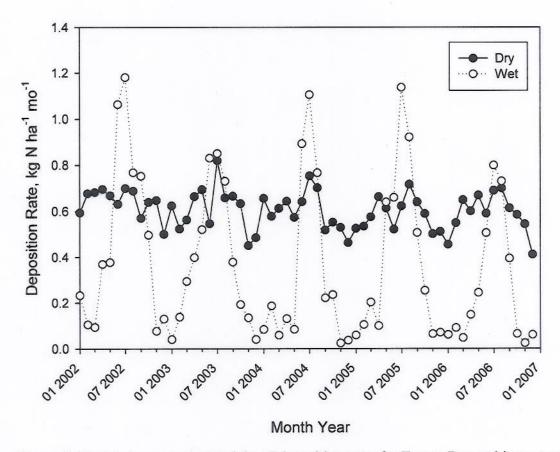


Figure 7. Modeled average wet and dry N deposition rates for Tampa Bay and its watershed.

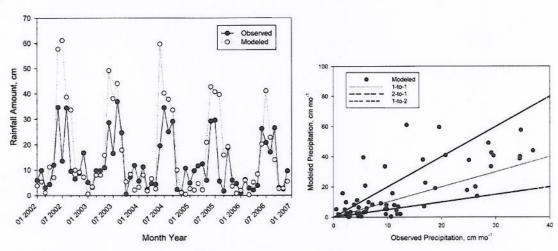


Figure 8. Comparison of CMAQ-modeled and observed precipitation rates for NADP's Verna Wellfield (FL41) site.

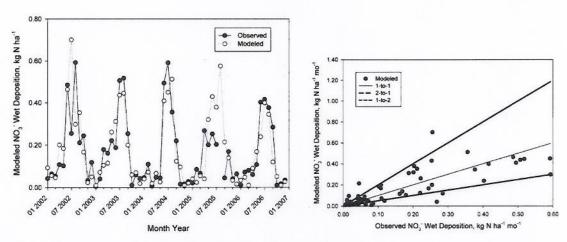


Figure 9. Comparison of CMAQ-modeled and observed NO₃ wet deposition rates for NADP's Verna Wellfield (FL41) site.

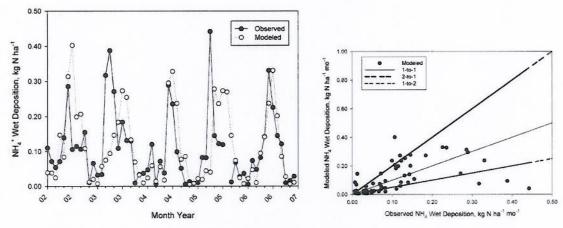


Figure 10. Comparison of CMAQ-modeled and observed NH₄⁺ wet deposition rates for NADP's Verna Wellfield (FL41) site.

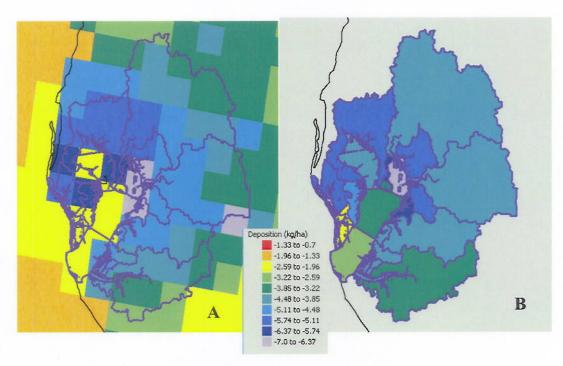


Figure 11. CMAQ-modeled changes in watershed N deposition for 2002 base case and 2020 future scenario emissions for Tampa Bay and its watershed, processed with WDT from CMAQ 2002 12-km gridded scale output. A: change in gridded N deposition rates (kg-N ha⁻¹); B: change in average N deposition rates by watershed basin and bay segment (kg-N ha⁻¹).