Trends in Atmospheric Reactive Nitrogen for the Eastern United States

Robert W. Pinder[a], K. Wyat Appel[a], Robin L. Dennis[a]

[a] *US Environmental Protection Agency, Office of Research and Development*

Abstract

Reactive nitrogen can travel far from emission sources and impact sensitive ecosystems. From 2002 – 2006, policy actions have led to decreases in NO_x emissions from power plants and motor vehicles. In this study, atmospheric chemical transport modeling demonstrates that these emissions reductions have led to a downward trend in ambient measurements of transported reactive nitrogen, especially atmospheric concentrations and wet deposition of nitrate. The trend in reduced nitrogen, namely ammonium, is ambiguous. As reduced nitrogen becomes a larger fraction of the reactive nitrogen budget, wide-spread NH_3 measurements and improved NH_3 emissions assessments are a critical need.

Capsule:

Ambient observations and simulation results indicate decreasing oxidized nitrogen levels over the Eastern US, but no trend in reduced nitrogen.

Keywords: reactive nitrogen, trends, atmospheric modeling

1. Introduction

In contrast to inert, diatomic N_2, atmospheric reactive nitrogen includes the forms of N that are chemically, biologically, or radiatively active. Due to the advent of the Haber-Bosch process and fossil fuel combustion, human production of reactive nitrogen has increased by an order of magnitude (Galloway et al., 2008). Oxidized nitrogen, such as NO_x, is largely emitted from combustion processes. When further oxidized to HNO_3, it rapidly deposits to surfaces. Reduced nitrogen, such as ammonia (NH_3), is emitted from agriculture and can combine with NO_3^- or other anions to form fine particles. These particles can be transported far from their source and deposit into

sensitive ecosystems. This can lead to soil acidification, loss of plant diversity, eutrophication, algal blooms, and loss of fish and shellfish (Paerl, 1997; Alexander et al., 2001).

Over the past decade, regulatory policies have been put in place to substantially reduce NO_x emissions. Accordingly, the US National Emission Inventory reports a steady decrease in NO_x emissions over the past decade (USEPA, 2008). However, emission trends are uncertain and should be critically examined using measurements (Parrish, 2006; Dallmann and Harley, 2010).

Several efforts have used measurements in North America to quantify the trend in NO_x concentration and have found large reductions that are most likely due to emissions. Recent work has attributed the decrease in urban NO_x concentrations in the US (Godowitch et al., 2010) and Canada (Geddes et al., 2009) over the past decade to reductions in vehicle NO_x emissions. Space-based measurements have observed large NO_2 reductions over the Ohio River Valley from 1999-2005 (Kim et al., 2006) as well as over urban areas in California from 2005-2008 (Russell et al., 2010).

In contrast to NO_x, there are few regulations relevant to NH_3 emissions. Atmospheric NH_3 concentration measurements in the Eastern US have been infrequent. Prior European assessments have demonstrated that interpreting the trend in reduced nitrogen without NH_3 measurements is challenging (Fowler et al., 2005; Fagerli and Aas, 2008).

Despite these challenges, our goal is to understand the trend in reactive nitrogen that is transported from emission sources to sensitive ecosystems. While prior work in the US has characterized trends near emission sources and urban areas, we will quantify the trends found in the ambient measurements of particles and wet deposition fluxes from regional monitoring networks. We will use an atmospheric chemistry and transport model to simulate the gas and particle phase transformations and ultimately, understand if the trends in the ambient measurements can be explained by the estimated trend in emissions.

2. Methods

2.1. Observations

To understand the trend in reactive nitrogen, we analyze monitoring networks designed to capture the gradient of concentration and deposition that

spans from emission sources to natural areas. This includes the Clean Air Status Trends Network (CASTNet) and the National Trends Network (NTN), part of the National Atmospheric Deposition Program. The location of the monitoring sites for both networks is shown in Figure 1.

CASTNet includes 69 sites in our modeling domain. Gas-phase nitric acid (HNO_3), particle nitrate (NO_3^-) and particle ammonium (NH_4^+) are measured using a three-stage filter pack that is collected and replaced every seven days. Because the seven-day sampling period can cause measurement artifacts, we compare our simulations to the total nitric acid, defined as $TNO_3 = HNO_3 + NO_3^-$. We do not compare NO_3^- during the warm season because the concentrations are low.

NTN measures weekly precipitation amount and the ammonium and nitrate precipitation concentration at 211 sites in our modeling domain. Our calculations are based on the deposition flux (kg ha^{-1}), defined as the product of the precipitation rate and the ammonium or nitrate concentration.

2.2. Atmospheric model

To understand if the trend in the observations is due to a trend in emissions, we use the Community Multi-scale Air Quality (CMAQ) model. The inputs to CMAQ are the anthropogenic emissions and meteorological conditions; outputs are concentrations and deposition fluxes for each hour of the simulation. CMAQ employs an Eulerian grid structure to explicitly simulate biogenic emissions, gas-phase, aqueous, and mixed-phase chemistry, advection and dispersion, aerosol thermodynamics and physics, and wet and dry deposition. A description and evaluation of the CMAQ processes is available in Foley et al. (2010) and the emissions and meteorological inputs are described in Appel et al. (2010). CMAQ has a high level of skill in modeling the inorganic aerosol system (Nolte et al., 2008) and capturing the interannual variability in wet deposition flux of nitrate and ammonium (Appel et al., 2010).

The simulations include two spatial domains – a 36 km horizontal resolution domain that includes all of the continental United States, and a 12 km horizontal resolution domain that spans from Maine to west Texas, as shown in Figure 1. We restrict our analysis to the more spatially-resolved 12 km domain and use the results of the 36 km domain as boundary conditions. The simulations use 24 vertical layers from the surface to 100 hPa.

2.3. Emissions databases

Quantifying the emission trends for our CMAQ simulation requires a different approach for each sector. At many power plants, NO_x emissions are directly measured. For vehicle emissions, we use the MOBILE6 model, which includes year specific estimates of vehicle miles traveled, fleet characteristics, and meteorological conditions. These two sectors are two-thirds of the total NO_x emissions, and have had large emission reductions over this period (Figure 2). Wildfire and soil NO_x emissions are derived from year-specific satellite fire counts and precipitation events, respectively. For other sources of NO_x, the emissions factors and activity data are not as well characterized (NARSTO, 2005), and we assume no change over this period.

Because NH_3 emissions are largely from livestock and fertilized fields (Pinder et al., 2006), and depend on specific farming practices and meteorological conditions, these emissions are even more uncertain (Beusen et al., 2008). Unlike reported NO_x emissions, indicators of NH_3 emissions, such as fertilizer use (`http://www.ers.usda.gov/Data/FertilizerUse/`), do not have the same downward trend. Our CMAQ simulations assume no change in NH_3 emissions over this time, except motor vehicle NH_3 as estimated by MOBILE6.

2.4. Defining trends

To calculate the trend in the observations and the simulations, we first pair the model and the observations in space and time. The data are averaged across all measurement sites for either the warm season (May – September) or the cold season (all other months). This distinction reflects the larger NO_x emission reductions from power plants during the warm season designed to mitigate ozone (USEPA, 2005). Linear regression is used to estimate the trend in the observations and model results as percent change per year. We also calculate p, the likelihood that the trend is not statistically different than zero. If p is greater than 0.1, there is at least a 10% chance that the trend is due to chance alone, and we report "no trend".

A confounding factor is that there are year-to-year differences in the weather that could obscure the trends. Using the criteria above, we do not find statistically significant trend in precipitation nor is there a trend in the CMAQ precipitation bias (Appel et al., 2010). Likewise, Godowitch et al. (2010) examined the year-to-year bias over this period in wind direction and mixing rates and concluded that year-to-year differences in the meteorology could not explain the trend in near-source NO_x concentrations.

3. Results and Discussion

The observed and modeled trends in concentrations and deposition of reactive nitrogen are shown in Table 1. The observations show statistically significant downward trends for oxidized nitrogen. However, for reduced nitrogen, CASTNet NH_4^+ concentrations have a decreasing trend, yet wet deposition flux measured at NTN sites do not show a trend. These trends and the extent to which they are captured by the CMAQ simulations is discussed below.

3.1. Trends in oxidized nitrogen

Both atmospheric concentration and wet deposition flux measurements of oxidized nitrogen show a statistically significant downward trend (Table 1). The warm season trends are larger than the cold season trends, due to the larger reduction in warm season emissions.

The warm season TNO_3 and wet deposition show a high level of correspondence between the CMAQ simulation and the measured trend. To explore this in more detail, Figure 3 shows the difference between 2006 and 2002 for CMAQ TNO_3 as measured at the CASTNet monitoring stations. The change in CMAQ matches the CASTNet observations at most locations, suggesting that the emission inputs and CMAQ simulation are capturing the spatial variability in the emission change and the resulting impact on atmospheric nitrate. Figure 4 shows the monthly averaged CMAQ TNO_3 and measurements at CASTNet. During winter, cooler temperatures cause more of the HNO_3 to be particle NO_3^- while the warm season has higher levels of gas-phase HNO_3. Because particle NO_3^- has a much lower rate of dry deposition and winter precipitation is less frequent, the concentration of TNO_3 increases in the winter. CMAQ is able to capture these seasonal differences, although the error increases in the fall and winter.

Compared to observations, the CMAQ-estimated trend has lower significance for cold season measurements of aerosol NO_3^-. This is likely because (1) the trend in emissions and measured concentrations is lower in the winter and (2) the partitioning between gas-phase and particle-phase is sensitive to larger uncertainties in the winter compared to the summer. The inorganic aerosol system is sensitive to NH_3 emissions and the role of heterogeneous chemistry in the rate of HNO_3 formation (Dennis et al., 2008). Both of these quantities are especially uncertain during wintertime (Gilliland et al., 2006; Davis et al., 2008).

Because precipitation efficiently scavenges both particle NO_3^- and gas-phase HNO_3, uncertainties in the aerosol partitioning have less of an impact on the CMAQ simulated trend. CMAQ accurately captures the trend in both warm and cold season NO_3^- wet deposition flux.

3.2. Trends in reduced nitrogen

Unlike oxidized nitrogen, the trends in reduced nitrogen are more ambiguous. The NTN measurements of NH_4^+ wet deposition flux and CMAQ simulation show no trend, yet the atmospheric NH_4^+ concentrations at CASTNet show a cold season downward trend, which is not replicated by CMAQ.

The decrease in CASTNet NH_4^+ concentration is likely due to decreases in emissions of other pollutants that influence the partitioning between NH_3 and NH_4^+. Previous studies studies of NH_4^+ trends in the US (Civerolo et al., 2010) and Europe (Fagerli and Aas, 2008) have found substantial dependence on sulfate (SO_4^{2-}). CASTNet measurements of SO_4^{2-} and NH_4^+ have a correlation of 0.85. However, from 2002 – 2006, there is no statistically significant trend in CASTNet SO_4^{2-} for either season, nor a trend for SO_2 emissions. There is a small downward trend in cold season NTN SO_4^{2-} deposition (-1.5% yr^{-1}). For the period 2002 – 2006, it is unlikely that sulfate changes alone are causing the NH_4^+ trend.

Because there has been no change in the NH_4^+ wet deposition flux and a substantial reduction in the NO_3^-, the simplest explanation is that the reduction in atmospheric NH_4^+ concentrations is due to a reduction in the availability of HNO_3, rather than a reduction in NH_3 emissions. This explanation is consistent with the CMAQ simulations, that have higher NH_3 in the gas-phase, increased NH_3 dry deposition flux, and less NH_4^+ in the particle phase.

4. Conclusions

Over the Eastern US, ambient measurements have found a substantial downward trend in indicators of oxidized nitrogen. CMAQ simulations show that this downward trend in TNO_3 and NO_3^- wet deposition can be explained by decreases in NO_x emissions.

Unlike oxidized nitrogen, the trend in reduced nitrogen is difficult to discern from ongoing measurements and CMAQ simulations. However, as reduced nitrogen becomes a larger fraction of the reactive nitrogen budget,

wide-spread NH_3 measurements and improved NH_3 emissions assessments are a critical need.

5. Acknowledgments

The authors thank Donna Schwede and two anonymous reviewers for helpful feedback. *Disclaimer*: Although this article has been reviewed by the EPA and approved for publication, it does not necessarily reflect EPA policies or views.

6. References

References

Alexander, R., Smith, R., Schwarz, G., Preston, S., Brakebill, J., Srinivasan, R., Pacheco, P., 2001. Nitrogen Loading in Coastal Water Bodies: An Atmospheric Perspective Coastal and Estuarine Studies. AGU press, Ch. Atmospheric Nitrogen Flux from the Watersheds of Major Estuaries of the United States: An Application of the SPARROW Watershed Model, pp. 119–132.

Appel, K. W., Foley, K. M., Bash, J. O., Pinder, R. W., Dennis, R. L., Allen, D. J., Pickering, K., 2010. A multi-resolution assessment of the Community Multiscale Air Quality (CMAQ) Model v4.7 wet deposition estimates for 2002 - 2006. Geoscientific Model Development Discussions 3 (4), 2315–2360.

Beusen, A., Bouwmana, A., Heuberger, P., Van Drecht, G., Van Der Hoek, K., 2008. Bottom-up uncertainty estimates of global ammonia emissions from global agricultural production systems. Atmospheric Environment 42, 6067–6077.

Civerolo, K., Hogrefe, C., Zalewsky, E., Hao, W., Sistla, G., Lynn, B., Rosenzweig, C., Kinney, P. L., 2010. Evaluation of an 18-year CMAQ simulation: Seasonal variations and long-term temporal changes in sulfate and nitrate. Atmospheric Environment 44 (31), 3745 – 3752.

Dallmann, T. R., Harley, R. A., 2010. Evaluation of mobile source emission trends in the United States. J. Geophys. Res. 115 (D14), D14305.

Davis, J. M., Bhave, P. V., Foley, K. M., 2008. Parameterization of n_2o_5 reaction probabilities on the surface of particles containing ammonium, sulfate, and nitrate. Atmospheric Chemistry and Physics 8 (17), 5295–5311.

Dennis, R. L., Bhave, P. V., Pinder, R. W., 2008. Observable indicators of the sensitivity of PM2.5 nitrate to emission reductions–Part II: Sensitivity to errors in total ammonia and total nitrate of the CMAQ-predicted non-linear effect of SO_2 emission reductions. Atmospheric Environment 42 (6), 1287 – 1300.

Fagerli, H., Aas, W., 2008. Trends of nitrogen in air and precipitation: Model results and observations at EMEP sites in Europe, 1980-2003. Environmental Pollution 154 (3), 448 – 461, reduced Nitrogen in Ecology and the Environment.

Foley, K. M., Roselle, S. J., Appel, K. W., Bhave, P. V., Pleim, J. E., Otte, T. L., Mathur, R., Sarwar, G., Young, J. O., Gilliam, R. C., Nolte, C. G., Kelly, J. T., Gilliland, A. B., Bash, J. O., 2010. Incremental testing of the Community Multiscale Air Quality (CMAQ) modeling system version 4.7. Geoscientific Model Development 3 (1), 205–226.

Fowler, D., Smith, R., Muller, J., Hayman, G., Vincent, K., 2005. Changes in the atmospheric deposition of acidifying compounds in the UK between 1986 and 2001. Environmental Pollution 137 (1), 15 – 25, recovery from acidificationin the UK: Evidence from 15 years of acid waters monitoring.

Galloway, J. N., Townsend, A. R., Erisman, J. W., Bekunda, M., Cai, Z., Freney, J. R., Martinelli, L. A., Seitzinger, S. P., Sutton, M. A., 2008. Transformation of the Nitrogen Cycle: Recent Trends, Questions, and Potential Solutions. Science 320 (5878), 889–892.

Geddes, J. A., Murphy, J. G., Wang, D. K., 2009. Long term changes in nitrogen oxides and volatile organic compounds in Toronto and the challenges facing local ozone control. Atmospheric Environment 43 (21), 3407 – 3415.

Gilliland, A. B., Appel, K. W., Pinder, R. W., Dennis, R. L., 2006. Seasonal NH_3 emissions for the continental United States: Inverse model estimation and evaluation. Atmospheric Environment 40 (26), 4986 – 4998, special

issue on Model Evaluation: Evaluation of Urban and Regional Eulerian Air Quality Models.

Godowitch, J. M., Pouliot, G. A., Rao, S. T., 2010. Assessing multi-year changes in modeled and observed urban NO_x concentrations from a dynamic model evaluation perspective. Atmospheric Environment 44 (24), 2894 – 2901.

Kim, S. W., Heckel, A., McKeen, S. A., Frost, G. J., Hsie, E. Y., Trainer, M. K., Richter, A., Burrows, J. P., Peckham, S. E., Grell, G. A., 2006. Satellite-observed US power plant NO_x emission reductions and their impact on air quality. Geophysical Research Letters 33 (22).

NARSTO, August 2005. Improving Emission Inventories for Effective Air Quality Management Across North America. Tech. Rep. NARSTO 05-001, NARSTO Emission Inventory Assessment Team.

Nolte, C. G., Bhave, P. V., Arnold, J. R., Dennis, R. L., Zhang, K. M., Wexler, A. S., 2008. Modeling urban and regional aerosols–Application of the CMAQ-UCD Aerosol Model to Tampa, a coastal urban site. Atmospheric Environment 42 (13), 3179 – 3191.

Paerl, H. W., 1997. Coastal eutrophication and harmful algal blooms: Importance of atmospheric deposition and groundwater as "new" nitrogen and other nutrient sources. Limnology and Oceanography 42 (5), 1154–1165.

Parrish, D. D., 2006. Critical evaluation of US on-road vehicle emission inventories. Atmospheric Environment 40 (13), 2288 – 2300.

Pinder, R. W., Adams, P. J., Pandis, S. N., Gilliland, A. B., 2006. Temporally resolved ammonia emission inventories: Current estimates, evaluation tools, and measurement needs. J. Geophys. Res. 111 (D16), D16310.

Russell, A. R., Valin, L. C., Bucsela, E. J., Wenig, M. O., Cohen, R. C., 2010. Space-based Constraints on Spatial and Temporal Patterns of NO_x Emissions in California, 2005-2008. Environmental Science and Technology 44 (9), 3608–3615.

USEPA, 2005. Evaluating Ozone Control Programs in the Eastern United States: Focus on the NO_x Budget Trading Program, 2004. Tech. Rep. EPA-454-K-05-001, US Environmental Protection Agency.

Figure 1: The CMAQ 36 km modeling domain (outer map), the 12 km domain used in this analysis (grey) and CASTNet (black) and NTN (white) sites used for this analysis. Note that some CASTNet and NTN sites are co-located.

Figure 2: The National Emission Inventory reports a decrease in NO_x emissions from power plants and vehicles (two-thirds of the total), but indicators of NH_3 emissions (fertilizer use) do not have a downward trend.

283 USEPA, January 2008. Latest findings on national air quality, status and
284 trends through 2006. Tech. Rep. EPA-454/R-07-007, U.S. Environmental
285 Protection Agency.

Figure 3: Warm season averaged CMAQ and CASTNet (circles) change in total nitrate from 2002 to 2006.

Figure 4: Monthly averaged CMAQ (blue) and CASTNet (black) total nitrate concentration. Grey vertical lines denote January.

Table 1: Summary of trends in reactive nitrogen, as observed and as modeled by CMAQ. If there is a least a 10% chance that the trend is due to chance alone, we report "no trend" ($p > 0.1$).

	Observations % change per year	Observations Trend Significance Level (p)	CMAQ % change per year	CMAQ Trend Significance Level (p)
Air Concentration				
CASTNet TNO_3				
warm season	-6.4%	0.001	-4.8%	0.001
cold season	-1.7%	0.1	-1.1%	0.1
CASTNet NO_3^-				
cold season	-2.3%	0.01	-1.5%	0.1
CASTNet NH_4^+				
warm season	no trend	—	no trend	—
cold season	-1.9%	0.1	no trend	—
Wet Deposition				
NTN NO_3^-				
warm season	-3.2%	0.001	-3.6%	0.01
cold season	-2.7%	0.001	-2.7%	0.01
NTN NH_4^+				
warm season	no trend	—	no trend	—
cold season	no trend	—	no trend	—
Dry deposition				
Oxidized N				
warm season	direct		-2.0%	0.001
cold season	measurements		-1.0%	0.01
Reduced N	are			
warm season	not		1.1%	0.01
cold season	available		1.1%	0.01

Figure 1
Click here to download Figure: Figure1.eps

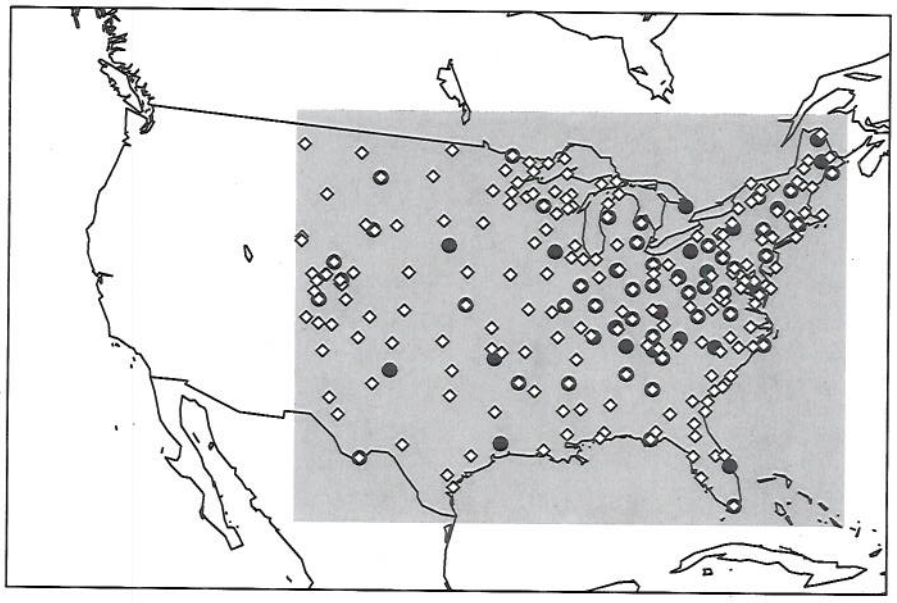

Figure 2
Click here to download Figure: Figure2.eps

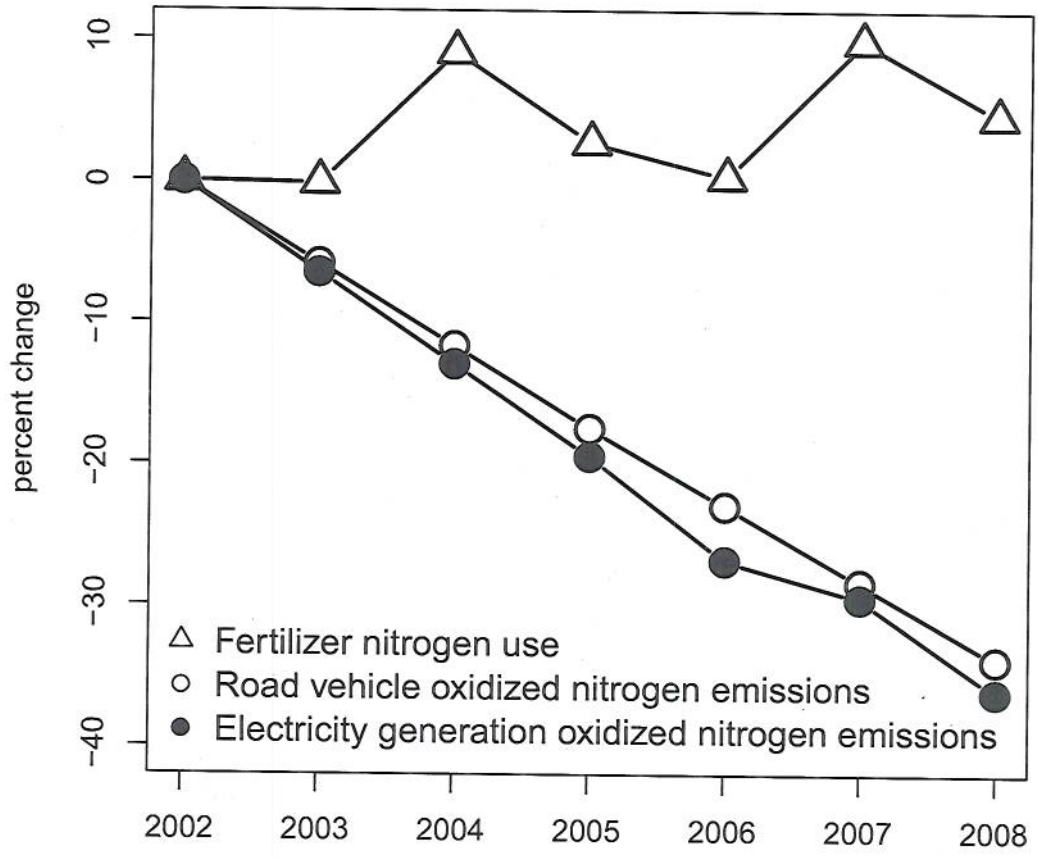

Figure3
Click here to download high resolution image

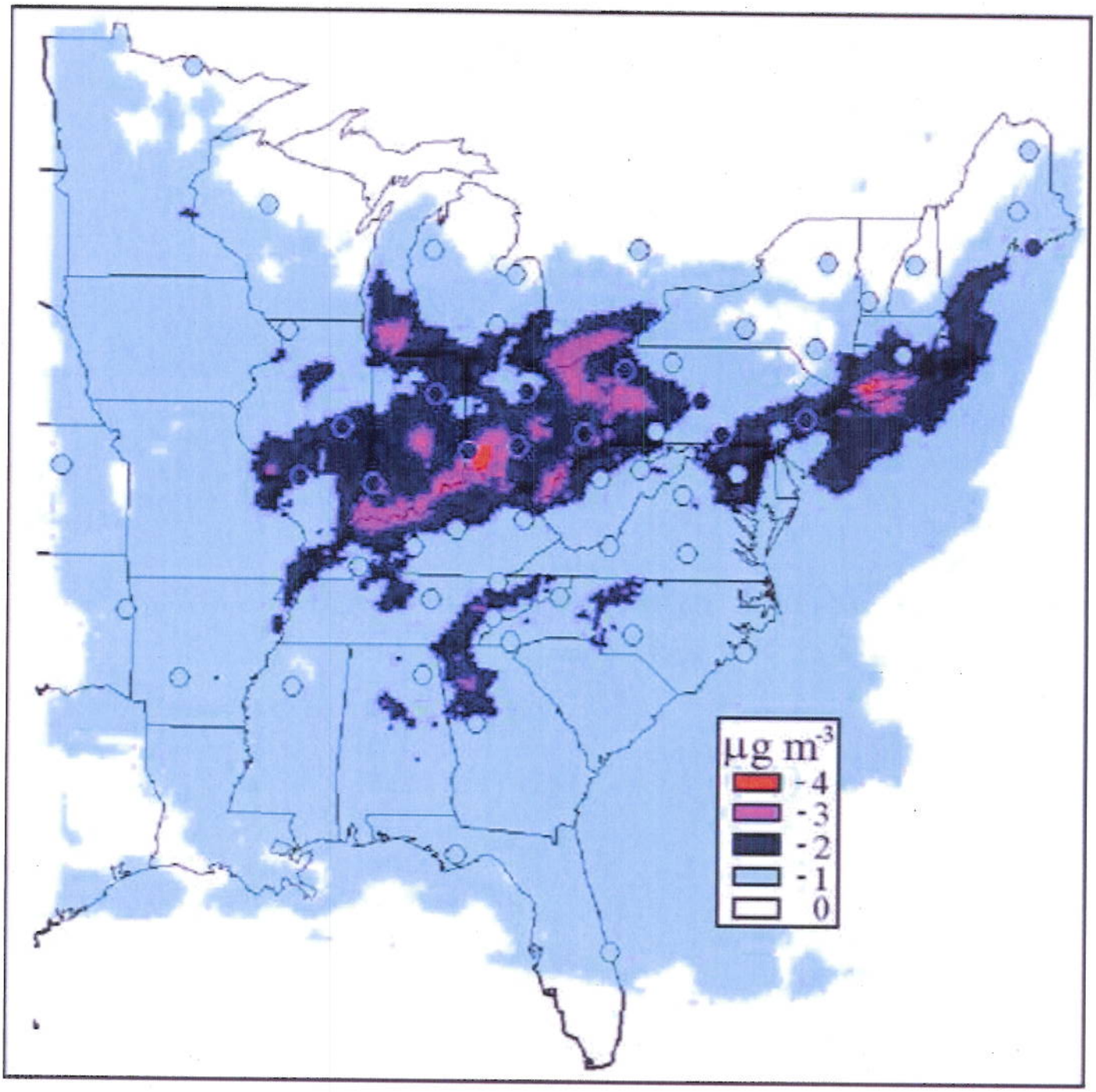

Figure 4
Click here to download Figure: Figure4.eps