Ammonia emission abatement does not fully control reduced forms of nitrogen deposition

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Contributed by John H. Seinfeld, February 28, 2020 (sent for review November 15, 2019; reviewed by Jeffrey Lee Collett Jr and Maria Kanakidou)

Human activities and population growth have increased the natural burden of reactive nitrogen (N) in the environment. Excessive N deposition on Earth’s surface leads to adverse feedbacks on ecosystems and humans. Similar to that of air pollution, emission control is recognized as an efficient means to control acid deposition. Control of nitrogen oxides (NOx = NO + NO2) emissions has led to reduction in deposition of oxidized nitrogen (NOy, the sum of all oxidized nitrogen species, except nitrous oxide [N2O]). Reduced forms of nitrogen (NHx = ammonia [NH3] + ammonium [NH4+]) deposition have, otherwise, increased, offsetting the benefit of reduction in NOx deposition. Stringent control of NH3 emissions is being considered. In this study, we assess the response of N deposition to N emission control on continental regions. We show that significant reduction of NH3 deposition is unlikely to be achieved at the early stages of implementing NH3 emission abatement. Per-unit NH3 emission abatement is shown to result in only 60–80% reduction in NH3 deposition, which is significantly lower than the demonstrated 80–120% benefit of controlling NOx emissions on NOx deposition. This 60–80% effectiveness of NH3 deposition reduction per unit NH3 emission abatement reflects, in part, the effects of simultaneous reductions in NOx and SO2 emissions.

Atmospheric deposition is the principal pathway for the exchange of nitrogen (N) between Earth’s compartments. Elevated N deposition on Earth’s surface has occurred (1–5), due to increasing human consumption of energy, with estimates of continuing growth in the near future (1, 3, 4, 6, 7). However, future increases of N deposition depend largely on the projection of future N emissions, which in some cases show slowdown or even stabilization trends (1). Response to excessive N deposition is exhibited mainly by eutrophication and acidification of terrestrial and aquatic ecosystems (8–11). The well-studied influences are damage and toxicity to vegetation and soil systems (12), impact on natural dominant species (13, 14), and even loss of ecosystem biodiversity (15). Therefore, prevention of excessive atmospheric N deposition is of vital importance in the protection of a sustainable ecosystem and in avoiding irreversible future damages.

Implementation of emission controls is an effective avenue to reduce acid deposition (3, 16–18). In the United States, oxidized nitrogen (NOx, sum of all oxidized nitrogen species except nitrous oxide [N2O]), deposition, a result of nitrogen oxides (NOx = NO + NO2) emissions from combustion, has been reduced since implementation of the Clean Air Act (CAA) in the 1970s. Nonetheless, rapid growth of the deposition of reduced forms of nitrogen (NHx = ammonia [NH3] + ammonium [NH4+]) has taken place (19) and offsets the benefits of NOx deposition reduction. NHx deposition results from wet deposition (precipitation) and dry deposition (driven by turbulent and molecular diffusion processes that bring NH3 into contact with surfaces) of gaseous NH3 and particulate NH4+. Relatively few studies have examined the effect of reducing NH3 emissions on NHx deposition. However, the effectiveness of NH3 emission abatement on reducing airborne fine-particle levels has proven lower than expected (20–23), since conversion between NH3 and NH4+ particulate matter is highly dependent on acidic aerosol components such as sulfate (SO42−) and nitrate (NO3−). A similar situation is likely to arise associated with the control of NH3 deposition.

Here, we address the impact of adding NH3 emissions control to NOx and SO2 emission control as a means to reduce NHx deposition over continental regions, as well as a comparison with the benefit of NOx emission abatement on reducing NOx deposition. We first review the consistency between the spatiotemporal trends of NH3 emissions and NHx deposition over the conterminous United States (CONUS) based on both national data and site measurement data. Then, we examine the response of NHx deposition to controlling NH3 emissions via modeling analysis of emission control scenarios.

Results and Discussion

Temporal Changes of N Emissions and N Deposition. We analyzed the temporal trends of N emissions, N wet deposition, and NO2 concentration with measured data in nine regions of CONUS from 2000 to 2017 (Fig. 1). Site measurements of NH3 ambient concentrations are available after 2007, but the numbers of sites in regions (SI Appendix, Table S1) are considerably lower than those of NO2 ambient concentration and N deposition (SI Appendix, Table S2), especially before 2011. Thus, temporal trends of NH3 ambient concentration are not included in Fig. 1.

Significance

Control of nitrogen oxides emissions has successfully reduced the deposition of oxidized nitrogen over the United States. Recent studies have called attention to the rapid growth of deposition of reduced forms of nitrogen, which would offset the benefits of reduction in oxidized nitrogen deposition. Our analysis, based on both monitoring and modeling approaches, illustrates that implementing ammonia emission abatement may not lead to full response in nitrogen deposition over continental regions. Here we provide important information to the community and policy makers concerning nitrogen deposition, given the urgent needs for developing control strategies on ammonia emissions.

Author contributions: J.T. and J.S.F. designed research; J.T. performed research; J.T. analyzed data; and J.T., J.S.F., and J.H.S. wrote the paper.

Reviewers: J.L.C., Colorado State University; and M.K., University of Crete. The authors declare no competing interest.

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This article contains supporting information online at https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.1920068117/-/DCSupplemental.

but are shown with the trends of N emission and deposition in SI Appendix, Fig. S1. NO$_3^-$ and NH$_4^+$ wet deposition and ambient NO$_2$ concentration are annual average values over all sites in the regions. NO$_x$ and NH$_3$ emissions are state-level values derived from the National Emissions Inventory (NEI) (see Materials and Methods for details).

NO$_x$ emissions (Fig. 1B, red line) peaked in 2002 in all CONUS regions, with amounts dropping by ~10% each year following for most regions, except the Northern Rockies and Plains (hereafter denoted Rockies) and the Southwest. This reduction of NO$_x$ emissions, associated with implementation of regulations and policies subsequent to the 1970 CAA, is reflected in the reduction of NO$_2$ levels (Fig. 1B, red X’s). NO$_3^-$ wet deposition (Fig. 1B, red bars) also started to decrease after 2002 in all regions, although levels in all regions did not decrease at the same rate. For instance, 7 y were required for the Rockies to show a significant decrease of NO$_3^-$ wet deposition, while clear and rapid (1–2 y after 2002) responses were found in the Upper Midwest, Northeast, South, and Central United States. Response times between decreases of NO$_x$ emissions and NO$_3^-$ wet deposition were associated with the reduction rates of NO$_x$ emissions, and the atmospheric acidity and humidity (23–25), which determine the gas-aerosol partitioning of NO$_3^-$.

Overall, clear consistency exists between changes of NO$_x$ emissions and NO$_3^-$ wet deposition in the temporal trends in all regions. The relationship between NH$_3$ emissions and NH$_4^+$ wet deposition, on the other hand, is considerably more complex than that between NO$_x$ emissions and NO$_3^-$ deposition. For example, a decrease in NH$_4^+$ wet deposition occurred during an increase of NH$_3$ emissions during 2004–2012 in the Upper Midwest (Fig. 1B, c). As well, with continuously decreasing NH$_3$ emissions after 2006 (Fig. 1B, d), the Northeast continued to experience increases in NH$_4^+$ wet deposition after 2011. Increases occurred in NH$_3$ airborne concentration in the Central and Northeast regions during 2011–2014 when NO$_x$ and NH$_3$ emissions and NO$_3^-$ and NH$_4^+$ wet deposition were decreased (SI Appendix, Fig. S1). The increased NH$_3$ air concentration is likely caused by release of NH$_4^+$ from the aerosol phase as SO$_4^{2-}$ and NO$_3^-$ concentrations and associated aerosol water decreased. Generally, it is difficult to establish a clear relationship between the trends of NH$_3$ emissions and NH$_4^+$ wet deposition.

Temporal changes of NO$_3^-$ wet deposition exhibited strongly positive linear correlations with those of NO$_x$ emissions for several regions, such as Northeast, Central, and South United States (Fig. 2A), with correlations (R values) between these trends of ~0.8 (Fig. 2C, green bars). On the other hand, correlations between NH$_3$ emissions and NH$_4^+$ wet deposition were either unclear (Central, Rockies, South, Southeast, and West) or weakly negative (Northeast, Northwest, Southwest, and Upper Midwest) (Fig. 2B). Moreover, R values between the trends were low (Fig. 2C, blue bars).
Spatial Changes of N Emissions and N Deposition. Spatial distributions of percentage changes in N emissions and N deposition (wet + dry) from 2001 to 2010 are shown in Fig. 3. Annual maps of N deposition were developed by combining the site observation data with deposition fields simulated by a chemical transport model provided by the Total Deposition Science Committee (TDEP) of the National Atmospheric Deposition Program (NADP) (Materials and Methods). Over this period, NOx emissions (Fig. 3A) decreased by 15–30% over CONUS, with slight increases in some regions, such as Montana (MT) and Nevada (NV). NOy deposition responses (Fig. 3B) were generally consistent with the changes in NOx emissions in both amount and distribution. NH3 emissions (Fig. 3C) increased by 10–30% over CONUS, whereas NHx deposition (Fig. 3D) exhibited mixed responses in different states. We found that the locations of areas with increased NHx deposition agreed well with areas of increased NOy deposition (Fig. 3B, contours with yellow and orange) and increased S deposition (SI Appendix, Fig. S2) in large extended regions around the states of MT, California (CA), Nebraska (NE), and Texas (TX). Changes in NH4+ wet
Response of NO\textsubscript{y} deposition to controlling NO\textsubscript{x} emissions. The response of NO\textsubscript{y} deposition to controlling NO\textsubscript{x} emissions (Fig. 4A) generally ranged from 80 to 120% over most CONUS regions. The ±20% variation around 100% could be a result of meteorological factors such as precipitation and long-range transport, in agreement with findings from Hemispheric Transport of Air Pollution, second phase (HTAP II) simulations (25), and could be viewed as impacts of long-term climate change. Some areas in MT, South Dakota (SD), and NE exhibited extraordinary values (~200%) (Fig. 4A, rust color), owing to very low (<5%) reductions in NO\textsubscript{x} emissions (SI Appendix, Fig. S3A). Overall, the average Res value of NO\textsubscript{y} deposition approached the ideal value of 100%.

The response of NH\textsubscript{3} deposition to controlling NO\textsubscript{x} emissions (Fig. 4B) was decreased by 30%, and would increase about 15% (seasonal variations) when NH\textsubscript{3} emissions were reduced by 30%. The compensation can be viewed as a buffering effect that weakens the sensitivity of NH\textsubscript{x} deposition to NH\textsubscript{3} emission change. It is concluded that significant reduction of NH\textsubscript{x} deposition is not likely to emerge in the early stage of NH\textsubscript{3} emission control. Our modeling results estimate that a 60–80% reduction of NH\textsubscript{x} deposition can be achieved per unit of NH\textsubscript{3} emission control, considerably lower than the full benefits of controlling NO\textsubscript{x} emissions to reduce NO\textsubscript{y} deposition. The management of NH\textsubscript{x} deposition is likely to be a focus for many regions in the near future. This “weakened” sensitivity needs to be taken into consideration

\[ \text{Res} = \frac{\text{Predicted } \% \text{ change of NO}_y \text{ or NH}_x \text{ deposition under emission changes over continental regions}}{\text{Predicted } \% \text{ change of NO}_y \text{ or NH}_x \text{ emissions under emission changes over continental regions}} \]  

The sensitivity of NH\textsubscript{x} dry deposition to NH\textsubscript{3} emission reduction is not included in the present study. Vegetation can serve as either a sink or source of atmospheric NH\textsubscript{3} depending on the balance between the NH\textsubscript{3} concentrations in the atmosphere and those in the stomata of leaves, which is referred to as the compensation point (28). This bidirectional NH\textsubscript{3} flux can increase the model prediction of NH\textsubscript{3} emission flux by 0–70% (29). It also increased the model prediction of NH\textsubscript{3} air concentration by 0–75%, with high influences during June–October and low impacts during December–February (30). A modeling study employing the Long Term Ozone Simulation–European Operational Smog (LOTOS-EUROS) model (31) with compensation point found that NH\textsubscript{3} dry deposition flux would only decrease about 10–15% (seasonal variations) when NH\textsubscript{3} emissions were decreased by 30%, and would increase about 15–25% when NH\textsubscript{3} emissions were increased by 30%. The compensation can be viewed as a buffering effect that weakens the sensitivity of NH\textsubscript{x} dry deposition to NH\textsubscript{3} emission change.

**Implications and Summary.** Despite a tight connection between NO\textsubscript{y} deposition and NO\textsubscript{x} emissions, such a strong relationship does not exist between NH\textsubscript{3} emissions and NH\textsubscript{x} deposition. In this study we controlled the emissions of SO\textsubscript{2}, NO\textsubscript{x}, and NH\textsubscript{3} simultaneously. It mimicked the situation that we are likely to face in the future, in which NO\textsubscript{x} and SO\textsubscript{2} emission control strategies remain in effect. As NH\textsubscript{x} deposition increased, NH\textsubscript{3} emission control was added to the existing control policies. We find that NH\textsubscript{x} deposition would resist decrease after NH\textsubscript{3} emissions are reduced. Reduction in SO\textsubscript{2} and NO\textsubscript{x} emissions leads to reduction of aerosol SO\textsubscript{4}\textsuperscript{2–} and NO\textsubscript{3}– but also to reduction in the associated aerosol water; thus, the level of acidity does not change appreciably (24). The overall result is promotion of the release of NH\textsubscript{4}+ to the gas phase, which increases the dry deposition of NH\textsubscript{x}.

**Fig. 4.** Predicted responses of N deposition (wet plus dry) to N emissions abatement in 2010. (A) Response of NO\textsubscript{y} deposition to NO\textsubscript{x} emission control. (B) Response of NH\textsubscript{x} deposition to NH\textsubscript{3} emissions control.
when developing control strategies for NH₃ emissions. The results of the present study for the United States are likely applicable to regions with intensive NH₃ deposition rates, such as India, and regions in which the dominant deposition components are in transition from NOₓ to NH₃ such as Europe.

**Materials and Methods**

Site observations of wet NOₓ deposition and wet NH₄⁺ deposition were provided by the National Trends Network (NTN) of the NADP (http://nadp.siwh.wisc.edu/NTN/). NTN measured the wet deposition at 373 sites located throughout the entire United States (SI Appendix, Fig. S4) from 1980s until present day. This study used the annual accumulated wet deposition data from 244 sites with available data in the study period (SI Appendix, Table S2). Site observations of airborne NO₂ concentrations were provided by Air Quality Monitoring Network of US Environmental Protection Agency (US EPA) (https://www.epa.gov/air-trends/nitrogen-dioxide-trends) (SI Appendix, Figs. S5 and S5 Table). Spatial distributions of NOₓ and NH₃ deposition were developed by the TDEP by spatial interpolation of quality-controlled observation sites with model simulations (http://nadp.siwh.wisc.edu/NTN/maps.aspx). Annual amounts of NOₓ and NH₃ emissions were provided by US EPA's NEI (https://www.epa.gov/air-emissions-inventories/national-emissions-inventory-nei). Spatial distributions of emissions were obtained from the Emissions Database for Global Atmospheric Research (EDGARv4.3.2) (https://edgar.jrc.ec.europa.eu/overview.php?v=432) at 0.1° resolution (∼11.1 km × 11.1 km). The EDGAR emissions over CONUS were developed based on information from US EPA's NEI (32).


The responses of deposition to emission changes were determined from simulated NOₓ and NH₃ deposition from multimodel mean (MMM) results of 11 global climate models from HTAP II, directed by the United Nations Economic Commission for Europe (http://www.htap.org/) (33). The models used were CAM-Chem, CHASER, rel. CHASER_r100, EMEP_rv48, GEMMACH, GEOS5, GEOSCHEM/AOJNT, OsloCTM3v2, GOCARTv5, SPRINTARS, and C-IFS_v2. Simulations were conducted for 2010, with an additional 6 mo as spin-up. The modeled NOₓ deposition comprises deposition of NOₓ, HNO₃, aerosol NO₃⁻, peroxycyano nitrate (PAN), and organic nitrates other than PAN. PAN performance on wet deposition of NOₓ and NH₃ was evaluated with the NADP observation network (ref. 5 and SI Appendix, Fig. S6). Simulation of dry deposition is subject to uncertainty, owing to lack of comprehensive observation data (5, 34). The base case utilized the HTAP v2.2 emissions inventory (35). In the emission control scenario, a modified emissions inventory was used with 20% reduction of all anthropogenic emissions, including SO₂, NOₓ, and NH₃ over North America. Since the meteorological fields and model parameters remained unchanged in the base case and control scenarios, emissions change is the main factor contributing to the variation of deposition.

**Data Availability.** All data are publicly available. Details about measurement data, emission, and modeling datasets are given in SI Appendix.

**ACKNOWLEDGMENTS.** We thank NADP and all participating modeling groups in HTAP II. We acknowledge the computational resources of the Oak Ridge National Laboratory, supported by the Office of Science of the US Department of Energy (Contract DE-AC05-00OR22725).

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**Data Repository:**
The data reported in this paper have been deposited in the Earth System Grid Federation, https://dx.doi.org/10.22033/ESGF-2019-002320

**Supporting Online Material:**
See the SI Appendix for supporting Online Material.

**Author Contributions:**


**Funding:**

This work was supported by the Ministry of the Environment of Japan, Grant-in-Aid for Global Environmental Research (Framework of the Global Environment Research Fund) 18016003, and the Global Environment Research Fund (19430812 and 18430702) Funds for the的目的.