

The Increasing Importance of U.S. Reduced Nitrogen Deposition

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Abstract

U.S. reactive nitrogen emissions increased greatly in the last century due to rapid increases in fossil fuel combustion and development of agriculture. One result was excess nitrogen deposition to many natural ecosystems. Successful policies in the last two decades to reduce nitrogen oxides emissions have substantially decreased nitrate wet deposition. Levels of wet ammonium deposition, however, have increased in many regions. Overall, the balance between oxidized and reduced nitrogen deposition has shifted from a nitrate-dominated situation in the 1980s to an ammonium-dominated situation today. Although gaseous ammonia has not historically been routinely measured in the U.S., a recent expansion in observations, combined with ongoing measurements of nitric acid and fine particle ammonium and nitrate, provides new insight into the balance of oxidized and reduced nitrogen in the total (wet + dry) U.S. nitrogen deposition budget. Observations reveal that reduced nitrogen contributes approximately 65 percent, on average, of the total inorganic nitrogen deposition budget. Dry deposition of ammonia plays an especially key role in nitrogen deposition. While U.S. emissions of nitrogen oxides are expected to continue to decline in the foreseeable future, ammonia emissions are projected to grow. Continued progress toward reducing U.S. nitrogen deposition will be increasingly difficult without new efforts to reduce ammonia emissions.

Keywords

ammonia, wet deposition, dry deposition, nitrate, bidirectional exchange

Introduction

Atmospheric reactive nitrogen sources are dominated by emissions of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) and ammonia (NH_3). NO_x is produced by high temperature processes including lightning, wildfires, and fossil fuel combustion. It reacts in the atmosphere to form nitric acid and other oxidized species. Ammonia also has both natural and anthropogenic sources. Within the U.S., agricultural activities including animal feeding operations and fertilizer application are the largest sources. Ammonia exists as a gas in the atmosphere and also can react with acidic compounds (e.g., nitric and sulfuric acids) to form fine particle salts. Both dry and wet deposition processes are active in removing gas and particle phase reactive nitrogen species from the atmosphere.

Anthropogenic reactive nitrogen emissions to the atmosphere accelerated rapidly in the 20th century in parallel with increased fossil fuel combustion and intensive agricultural activities (Galloway et al., 2008; Erisman et al., 2011; Liu et al., 2013). As concentrations grew, so did wet and dry deposition of reactive nitrogen to terrestrial and aquatic ecosystems. Although nitrogen is an important nutrient for ecosystems, increases in its deposition have raised concerns due to adverse environmental impacts. Critical loads (CLs) have been used to quantify levels of reactive nitrogen deposition that ecosystems can sustain without significant harmful effects. Twenty-four of the 45 national parks in the contiguous United States (U.S.) were estimated to receive reactive nitrogen deposition above the CL in 2013 (Ellis et al., 2013).

U.S. NO_x emissions have declined over the past two decades due to effective regulations designed to decrease NO_x contributions to ozone, fine particles, and acid deposition. Data from the National Emissions Inventory (NEI) Air Pollutant Emissions Trends (<http://www.epa.gov/ttnchie1/trends/>) indicate that NO_x emissions decreased by nearly 41% from 1990 to 2010. Future reductions are also expected. By contrast, NH_3 emissions have been reported to increase by 11% between 1990 and 2010 (Xing et al., 2013). Future ammonia emissions, which are currently unregulated in the U.S. as in many regions around the globe, are projected to further increase in coming decades (Ellis et al., 2013).

By examining long-term U.S. wet deposition records, we can examine the impact of NO_x and NH_3 emission changes on reactive nitrogen deposition via rain and snow. Specifically, we will examine changes in the balance between oxidized and reduced nitrogen contributions. Making use of recently expanded ammonia measurements, together with longer-term dry deposition records for gaseous nitric acid and fine particle ammonium and nitrate, we can for the first time also evaluate the relative oxidized and reduced nitrogen contributions to dry (and total) reactive nitrogen deposition and examine how they vary across the country.

Approach

Weekly precipitation concentrations of NH_4^+ and NO_3^- were obtained from the NADP National Trends Network (NTN; <http://nadp.isws.illinois.edu/ntn/>). Weekly gaseous HNO_3 concentrations and particulate NH_4^+ and NO_3^- concentrations were obtained from the Clean Air Status and Trends Network (CASTNET; <http://epa.gov/castnet/javaweb/index.html>). Bi-weekly concentrations of gaseous NH_3 were taken from the NADP Ammonia Monitoring Network (AMoN; <http://nadp.isws.illinois.edu/AMoN/>). To gain greater spatial coverage of airborne NH_3 concentrations, NH_x ($\text{NH}_3 + \text{NH}_4^+$) measurements from a pilot Interagency Monitoring of Protected Visual Environments (IMPROVE) NH_x monitoring network (Chen et al., 2014) were also used.

Wet N deposition was determined from the total precipitation and aqueous concentrations of NH_4^+ and NO_3^- . Dry N deposition was calculated as the product of a N species concentration and its deposition velocity. Deposition velocities of gaseous HNO_3 and particulate NH_4^+ and NO_3^- were provided by CASTNET for each of its measurement sites based upon the Multi-Layer Model (MLM) (Meyers et al., 1998), with input of on-site meteorology and local site characteristics. The deposition velocity of NH_3 is difficult to determine due to the bidirectional nature of its flux that depends strongly on local conditions (Massad et al., 2010). In order to estimate dry NH_3 deposition here, its deposition velocity was calculated as 70% of the HNO_3 deposition velocity following previous estimates (Beem et al., 2010; Benedict et al., 2013). A simple two-layer bidirectional flux modeling approach (Nemitz et al., 2001) was also implemented as another constraint on NH_3 dry deposition flux estimates. The bidirectional model employs hourly CASTNET meteorology and measured NH_3 concentrations to estimate NH_3 exchange with soil and vegetation, as well as net fluxes above the vegetation. Ammonia compensation points and leaf surface resistances were parameterized following the recommendations of Massad et al. (2010) for natural vegetation.

Results and Discussion

Wet N deposition was dominated by oxidized N (NO_3^-) across much of the country in the early 1990s. Most locations now receive a majority of their wet N deposition as reduced N (NH_4^+), a trend also recently reported by Du et al. (2014). In the early 1990s more than two-thirds of observation sites saw a majority of wet N deposition coming from oxidized N; twenty years later, more than two-thirds of sites saw a majority of wet N deposition from reduced N. This major shift reflects a combination of reductions in wet nitrate deposition in almost all U.S. states along with increases in wet ammonium deposition at many locations. These trends are broadly consistent with emissions trends discussed above for NO_x and NH_3 . In addition to changes in deposition, relative changes in NO_x and NH_3 emissions also alter the relative amounts of these compounds in the atmosphere; changes in both species have the potential to alter formation of fine particles, while changes in NO_x can affect the oxidation of atmospheric volatile organic compounds and influence production of oxidants such as ozone and hydrogen peroxide.

Dry and total (wet + dry) deposition estimates were calculated for 37 monitoring locations in eight U.S. geographic regions using the data sets and approaches outlined above. For the base case approach, where the ratio of ammonia to nitric acid deposition velocities is assumed to be 70%, reduced N deposition fractions at individual sites range from 38% (only one site is below 50%) to 81%. Reduced N deposition fractions in the eight regions range from 58% to 78%, with the lowest fraction in the Pacific Northwest and the highest contribution in the agriculturally intensive upper Midwest (see Figure 1). Dry NH_3 deposition alone contributed between 19% (Northwest) and 63% (Southwest) of the total budget. Spatial patterns of the reduced N deposition fraction generally reflect spatial variations in agricultural activity.

At the annual scale, NH_3 dry deposition rates estimated using the bidirectional model are typically about half those derived from the base approach, although there is large variability regionally. A reduction in net ammonia flux to the surface is expected when emission from the surface is considered. Additional work is

urgently needed, however, to evaluate the accuracy of this modeling approach across a range of ecosystems. Even with the significant reduction in ammonia dry deposition suggested by the bidirectional modeling approach outlined here, reduced nitrogen continues to comprise the majority of inorganic N deposition across the U.S.

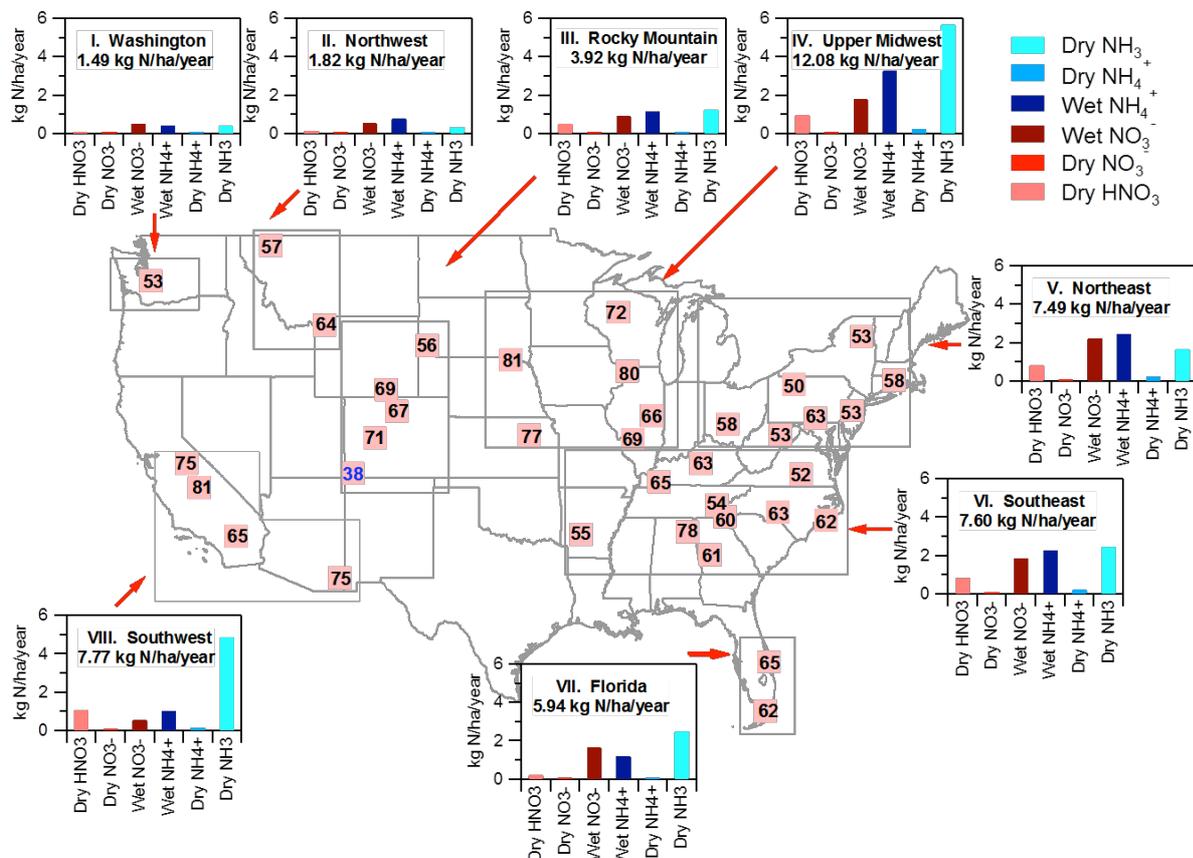


Figure 1. Reactive nitrogen deposition budgets for 37 U.S. locations in eight regions of the country. Included pathways are wet deposition of nitrate and ammonium and dry deposition of gaseous ammonia and nitric acid and fine particle ammonium and nitrate. The number provided at each site location indicates the percentage of wet+dry deposition coming from reduced nitrogen species (ammonia and ammonium). The panel for each region indicates the total annual reactive N deposition flux for the included pathways and the individual contributions from each pathway.

Conclusions

Increases in emissions of ammonia and the success of U.S. policies to decrease NO_x emissions over recent decades are changing the character of U.S. reactive nitrogen deposition. While U.S. wet inorganic N deposition was once dominated by nitrate, wet inorganic N deposition now comes mostly from ammonium at more than two-thirds of U.S. monitoring sites. While estimates of dry deposition fluxes of inorganic N contain more uncertainty, total (wet plus dry) deposition fluxes also appear to be dominated by reduced N in most parts of the country. Future wet deposition of nitrate is expected to continue decreasing, as U.S. NO_x emissions are further reduced. Projected increases in ammonia emissions, meanwhile, will drive future increases in deposition of reduced nitrogen. If the U.S. is to continue making progress toward decreasing wet and dry deposition of reactive N, it would be helpful to consider strategies for reducing ammonia emissions. Such a reduction could also yield other regional benefits through a decrease in fine particle concentrations and their associated contributions to haze and adverse human health effects.

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