Increasing importance of deposition of reduced nitrogen in the United States

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Rapid development of agriculture and fossil fuel combustion greatly increased US reactive nitrogen emissions to the atmosphere in the second half of the 20th century, resulting in excess nitrogen deposition to natural ecosystems. Recent efforts to lower nitrogen oxides emissions have substantially decreased nitrate wet deposition. Levels of wet ammonium deposition, by contrast, have increased in many regions. Together these changes have altered the balance between oxidized and reduced nitrogen deposition. Across most of the United States, wet deposition has transitioned from being nitrate-dominated in the 1980s to ammonium-dominated in recent years. Ammonia has historically not been routinely measured because there are no specific regulatory requirements for its measurement. Recent expansion in ammonia observations, however, along with ongoing measurements of nitric acid and fine particle ammonium and nitrate, permit new insight into the balance of oxidized and reduced nitrogen in the total (wet + dry) US nitrogen deposition budget. Observations from 37 sites reveal that reduced nitrogen contributes, on average, ~65% of the total inorganic nitrogen deposition budget. Dry deposition of ammonia plays an especially key role in nitrogen deposition, contributing from 19% to 65% in different regions. Future progress toward reducing US nitrogen deposition will be increasingly difficult without a reduction in ammonia emissions.

ammonia | dry deposition | wet deposition | nitrogen oxides | agriculture

Beginning in the mid-20th century, emissions of anthropogenic reactive nitrogen (N_r) to the atmosphere accelerated rapidly due to increased fossil fuel combustion and intensive agricultural activities (1–4). Once emitted to the atmosphere, N_r compounds are deposited to terrestrial and aquatic ecosystems through dry and wet processes. Although nitrogen is an essential and often limiting element for ecosystems, increases in N_r deposition resulting from increased emissions have raised concerns around the world due to its adverse environmental impacts, including decreased biological diversity, increased soil acidification, and lake eutrophication (5–9). Critical loads (CLs) have been widely used to quantify levels of N_r deposition that ecosystems can sustain without significant harmful effects (10, 11). Twenty-four of the 45 national parks in the contiguous United States were estimated to receive N_r deposition in 2013 exceeding the local CL (12). Atmospheric N_r (an important ingredient of ozone and fine particle formation) has also been linked with climate change and human health degradation (8, 13, 14).

Atmospheric N_r sources are dominated by emissions of nitrogen oxides ($NO_x = NO + NO_2$) and ammonia (NH_3) (8). NO_x is produced by a wide range of high temperature processes including lightning and the combustion of fossil fuels by vehicles, electric power generating units, and other industrial and natural combustion sources. NO_x is oxidized in the atmosphere and converted to a variety of forms, including nitric acid, with a short timescale (typically 1 d or less). Reis et al. (15) attributed more than 80% of the NH_3 emissions in the United States to the agricultural sector, including emissions from livestock waste and volatilization of N-based fertilizer.

During the last two decades, US NO_x emissions have steadily declined due to effective regulations designed to decrease NO_x contributions to ozone, fine particles, and acid deposition (16). Data from the National Emissions Inventory (NEI) Air Pollutant Emissions Trends (https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data) indicate that NO_x emissions decreased by nearly 41% from 1990 to 2010. Further reductions are expected in coming years due to additional policy actions (e.g., the Cross-State Air Pollution Rule, reductions in mobile source emissions, and 5-y reviews of the National Ambient Air Quality Standards). Meanwhile, NH_3 emissions have been reported to increase by 11% between 1990 and 2010 (17), with contributing factors including regional growth in livestock numbers and increased application of NO_x controls such as selective catalytic reduction. Unlike NO_x, NH_3 emissions in the United States are not regulated. In 2006, US anthropogenic NH_3 emissions were estimated at 2.8 Tg N/y; they are projected to increase to between 3.3 and 4.2 Tg N/y by 2050, mainly due to increases in N fertilizer application and livestock growth (12).

Significance

Human activities have greatly increased emissions of reactive forms of nitrogen to the atmosphere. This perturbation to the nitrogen cycle has produced large increases of nitrogen deposition to sensitive ecosystems. Over recent decades, attention has focused on wet and dry deposition of nitrate stemming from fossil fuel combustion emissions of nitrogen oxides. Successful decreases in nitrogen oxides emissions in the United States have substantially decreased nitrate deposition. By contrast, emissions of ammonia, an unregulated air pollutant, and resulting deposition of ammonium have grown. Expanded observations demonstrate that deposition of reactive nitrogen in the United States has shifted from a nitrate-dominated to an ammonium-dominated condition. Recognition of this shift is critical to formulating effective future policies to protect ecosystems from excess nitrogen deposition.

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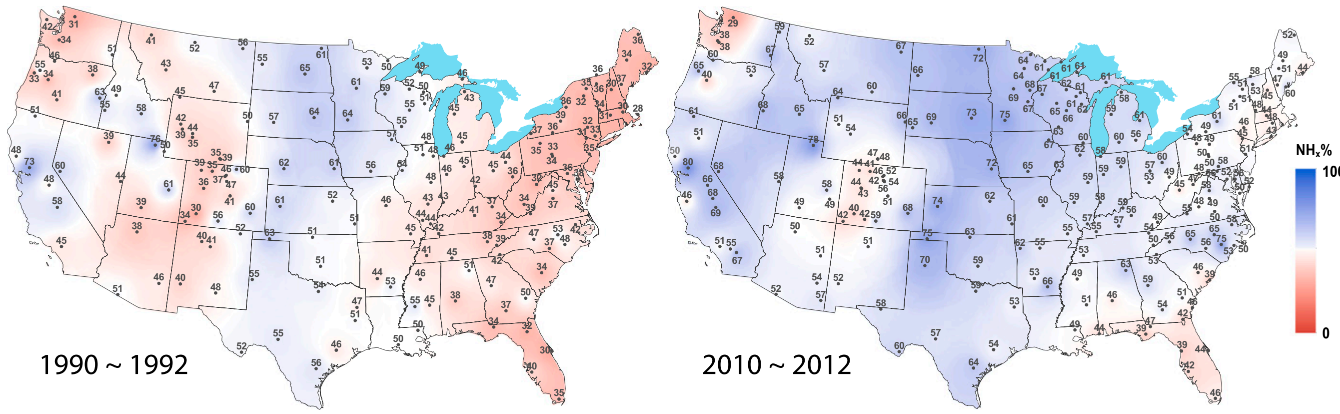

Fig. 1. Comparisons of the 3-y average NH_4^+ percentage of wet inorganic nitrogen deposition across the United States in 1990–1992 (*Left*) and 2010–2012 (*Right*). To help visualize spatial patterns, isopleths were produced by interpolating NH_4^+ mole percentages at individual monitoring sites using a cubic inverse-distance weighting of sites within 500 km of each observation station. The black dots on the map represent locations of sites with 3-y data available for each time period. The NH_4^+ percentage on a molar basis [$(NH_4^+\%) = (NH_4^+)/(NO_3^- + NH_4^+) \times 100\%$] is noted at each site.

Through dry deposition processes, gaseous HNO_3 and NH_3 are rapidly removed from the atmosphere and deposited to surface ecosystems. HNO_3 and NH_3 can both be incorporated into atmospheric particles; this includes their reaction with each other to form fine particle ammonium nitrate, reaction of ammonia with sulfuric acid to form fine particle ammonium sulfate, and reactions of nitric acid with soil dust or sea salt to form coarse particle nitrate (18), among other species. These aerosol particles can also deposit nitrate and/or ammonium via dry deposition. Nitric acid, ammonia, and particulate nitrate and ammonium are scavenged by clouds and precipitation, producing wet deposition of ammonium and nitrate. HNO_3 and NO_3^- are generally referred to as oxidized N, whereas NH_3 and NH_4^+ are termed reduced N; both oxidized and reduced N represent significant N_r inputs in unmanaged ecosystems (19, 20).

Publications from the 1990s and early 2000s recognized that deposition of oxidized N dominated the US atmospheric reactive N deposition budget (21, 22). With the ensuing emissions reductions of NO_x and emissions increases of NH_3, relative contributions of oxidized and reduced N have likely changed in recent years. Modeling studies (12, 23) have suggested this change and point to its likely continuation. A recent analysis of US National Atmospheric Deposition Program (NADP) observations (24) illustrates decreases in US wet nitrate deposition and increases in wet ammonium deposition in many regions. Focusing on the Midwest and Eastern United States, Sickles and Shadwick (25) reported that reductions in NO_x emissions have decreased oxidized nitrogen dry and wet deposition and that particulate ammonium concentrations now exceed concentrations of particulate nitrate plus gaseous nitric acid in the region. Ammonia gas was not considered in their study.

From an observational perspective, the absence of gaseous ammonia observations has prevented a broad, national understanding of the overall contributions of oxidized and reduced forms of inorganic N to the total N_r deposition budget. Making use of longer-term wet and dry deposition records and newly available NH_3 measurements from regions across the country, we examine the overall contributions of oxidized and reduced forms of inorganic nitrogen to wet, dry, and total deposition budgets to better inform discussions of strategies to decrease N deposition to sensitive ecosystems.

Results and Discussion

Analyses of wet deposition records provide important insight into the shift from oxidized to reduced nitrogen deposition across the contiguous United States. Recently expanded measurements of gas and particle phase reactive nitrogen species permit an assessment of current contributions of oxidized and reduced nitrogen to the US N_r dry deposition budget. By combining these analyses, we gain a better understanding of the importance of both oxidized and reduced nitrogen to the total (wet + dry) N_r deposition budget across much of the United States.

Oxidized vs. Reduced N in Wet N Deposition. Although 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^+) (Fig. 1), a trend also recently reported by Du et al. (24). During the period 1990–1992, 69% of the observation sites were subjected to oxidized N contributions in excess of 50%; 20 y later, 69% of the sites instead received wet deposition of reduced N greater than 50%.

Changes in fractional contributions of oxidized and reduced N depend on the combined changes in wet deposition fluxes of NH_4^+ and NO_3^-. Fig. 2 examines these changes for 45 of the 48 contiguous United States with available data. In every state but North Dakota, nitrate wet deposition fluxes decreased, with an average decrease of 29%. The nationwide decrease of oxidized N in wet deposition is consistent with the downward trend of US NO_x emissions. With the successful implementation of the Clean Air Act (CAA) and the 1990 Amendments, NO_x emissions were estimated to decline by 36% between 1990 and 2008 (13).

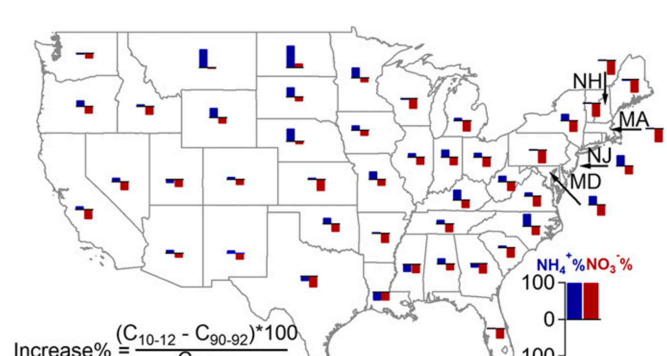

Fig. 2. Absolute percentage change of NH_4^+ and NO_3^- in wet deposition across the country. $C_{10–12}$ is the average NH_4^+ or NO_3^- flux (kg N/ha per year) in each state between 2010 and 2012 and $C_{90–92}$ is the average NH_4^+ or NO_3^- flux (kg N/ha per year) between 1990 and 1992. Only sites in Fig. 1 with both 1990–1992 and 2010–2012 data available are used to calculate the average flux for each state.

Nitrate wet deposition decreases were largest in the Northeastern United States, an area where large NO_x emissions reductions were implemented. Lehmann and Gay (26) examined trends in nitrate concentrations in US wet deposition in detail for a period ending in 2009 and also highlight large reductions in the Northeastern United States.

Thirty-seven of 45 states experienced increased ammonium wet deposition over the last two decades; for these states, the average increase was 22% (Fig. 2). Increases in ammonium wet deposition were especially common in the northern plains states; relatively large increases were also seen in North Carolina, Kentucky, Maryland, and New Jersey. Substantial increases in ammonium ion concentrations in precipitation in the Central and Western United States were previously reported through 2004 by Lehmann et al. (27). The increasing NH_4^+ wet deposition is broadly consistent with the estimates of increasing NH_3 emissions since the 1990s (17).

Oxidized vs. Reduced Dry Inorganic N Deposition. Gas phase nitric acid and ammonia and particulate ammonium and nitrate are potentially important contributors to dry inorganic N deposition. Limited historical measurements, especially for ammonia, prevent an analysis of long-term trends of oxidized vs. reduced dry inorganic nitrogen deposition like those presented above for wet deposition. Recent efforts to measure gas phase ammonia concentrations more routinely by the NADP Ammonia Monitoring Network (AMoN) and Interagency Monitoring of Protected Visual Environments (IMPROVE) NH_x networks, however, allow comparison of the current balance between oxidized and reduced inorganic N dry deposition. We focus here on characterizing spatial patterns for the period 2011–2013. Fig. 3 illustrates (by circle size) the current magnitude of dry inorganic N deposition across the United States. Significant spatial variability is seen from site to site, reflecting difference in species concentrations. Estimated annual sums of dry deposition by gaseous ammonia and nitric acid and particulate ammonium and nitrate range from 0.49 (WY08) to 13.4 kg N/ha per year (NE98). Reduced N contributes more than 50% of the total calculated dry inorganic N deposition at all sites except Mesa Verde National Park (CO99; 44%) in southwest Colorado. This remote arid site is expected to have relatively small agricultural impacts (28) but greater influence of NO_x emitted from nearby oil and gas development (29) and the large, coal-fired Four Corners and San Juan power plants. The highest fractional and absolute reduced N contributions are seen, not surprisingly, in areas with substantial agricultural activity, including sites in Illinois (IL37 exhibits the highest reduced N fraction at 90%), Nebraska, and the Central Valley of California.

To examine overall dry deposition patterns, sites were grouped into eight regions (by proximity and similar trends) as follows (Table S1 and Fig. 3): Washington (I), Northwest (II; Montana and northern Wyoming), Rocky Mountain (III; western South Dakota and southern Wyoming, CO), Upper Midwest (IV; Wisconsin, Illinois, eastern Kansas, and eastern Nebraska), Northeast (V; New York, Connecticut, New Jersey, Pennsylvania, Ohio, and West Virginia), Southeast (VI; Kentucky, Virginia, Tennessee, North Carolina, Georgia, Alabama, and Arkansas), Florida (VII), and Southwest (VIII; California and southern Arizona). The lowest regional average dry N deposition flux was found in the Washington region (0.51 kg N/ha per year) and the highest in the Upper Midwest (7.0 kg N/ha per year), one of the nation's primary food production areas with large NH_3 emissions from livestock and fertilizer use.

In most regions, dry ammonia and nitric acid deposition display strong seasonal patterns, with higher values in summer and lower values in winter. These seasonal patterns are driven mostly by seasonal concentration patterns rather than changes in deposition velocity. Ammonia emissions increase with warmer summertime temperatures due to enhanced volatilization (30, 31). Active summertime photochemistry speeds conversion of NO_x to nitric acid, whereas warmer summertime temperatures reduce formation of particulate ammonium nitrate, leaving more nitric acid and ammonia in the gas phase (32). Interestingly, dry NH_3 deposition is elevated during the winter in the Upper Midwest compared with other regions. Higher winter ammonia concentrations in this region might reflect trapping of cold season ammonia emissions (from livestock and/or winter fertilizer application) near the surface by a shallow boundary layer (28). Dry N deposition exhibits a winter seasonal maximum in Florida. Increased summertime precipitation

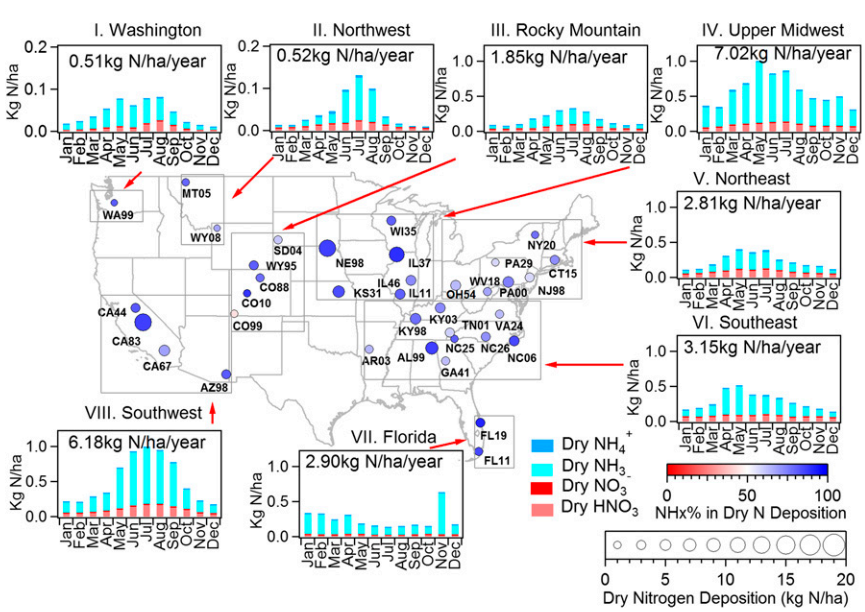

Fig. 3. Spatial and temporal trends in dry inorganic N deposition at 37 locations across the United States. Included are deposition of gaseous nitric acid and ammonia and $PM_{2.5}$ ammonium and nitrate. Fractional reduced N contributions are represented by circle color. The total deposition from these four species is indicated by circle size. The bar charts depict monthly average contributions of individual dry reduced and oxidized N deposition pathways for eight selected regions. The average total dry inorganic N deposition fluxes in different regions are shown by the number in each figure.

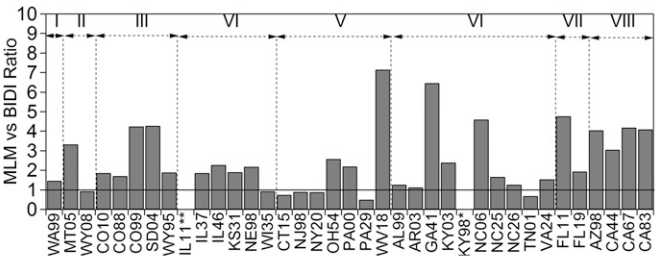

Fig. 4. Ratio of annual NH_3 dry deposition rates estimated using the MLM vs. bidirectional approaches. Regions are indicated at top of graph. *Due to a lack of meteorological data, the bidirectional flux model is not parameterized appropriately for site KY98. **Due to vegetation type, the bidirectional flux model is not parameterized appropriately for site IL11.

here suppresses summertime atmospheric concentrations and therefore dry deposition of reduced and oxidized N species. In Florida wet N deposition contributed more than 75% of total (wet + dry) inorganic N deposition during summer when there was more precipitation (Fig. S1); dry deposition of reduced N was the dominant input during the drier winter season.

At the annual scale, ammonia dry deposition rates estimated using the multilayer model (MLM) approach are larger than those derived from the bidirectional model by a factor of 1.90 (median MLM/bidirectional flux ratio of 35 sites listed in Fig. 4). A reduction in NH_3 dry deposition rates, relative to the unidirectional flux framework, was also observed on implementation of NH_3 bidirectionality in the Community Multiscale Air Quality Model (33). MLM vs. bidirectional model differences vary across regions but generally result from stomatal and ground compensation points, as well as the effects of surface acidity, represented in the bidirectional framework. The net result of these processes is to reduce the atmosphere-surface NH_3 concentration gradient, and therefore the flux, relative to the unidirectional MLM deposition velocity approach, which assumes a zero surface concentration. Model differences are generally greatest in summer (Fig. S2) when temperature driven stomatal and soil compensation points are at a maximum. On average, the bidirectional and MLM approaches yield comparable net fluxes during winter when compensation points are lowest and surfaces are more acidic. Further discussion of the MLM vs. the bidirectional model is included in *SI Methods*.

The relatively large overall differences between the MLM and bidirectional NH_3 flux estimates warrant brief discussion of the significant uncertainties that persist in modeling dry deposition of reactive nitrogen. MLM HNO_3 deposition velocities, on which the NH_3 deposition velocity used here is based, may contain up to ±25% uncertainty related to error in the measurements that drive the model and underlying process parameterizations (34). Models of HNO_3 deposition velocity also differ substantially themselves. For example, a multisite evaluation of the MLM and Big Leaf Model used in the Canadian Air and Precipitation Monitoring Network (CAPMoN) showed a median bias in hourly HNO_3 deposition velocities of −35%, with MLM yielding lower values (35). Regarding bidirectional NH_3 models, comparisons to average measured NH_3 fluxes over nonagricultural ecosystems generally demonstrate agreement within ±30% using site-specific process parameterizations (36–39), although differences can be much larger under specific meteorological and surface conditions. Uncertainty may also be significantly larger when applying generalized parameterizations as done here. In that regard, recent versions of bidirectional models (40–42) have not yet been rigorously compared with each other or against flux measurements for natural ecosystems in North America. Although our analyses use commonly used approaches for both HNO_3 deposition velocity and bidirectional NH_3 flux, the abovementioned uncertainties are included to emphasize that the dry deposition component of the N deposition budget is significantly more uncertain

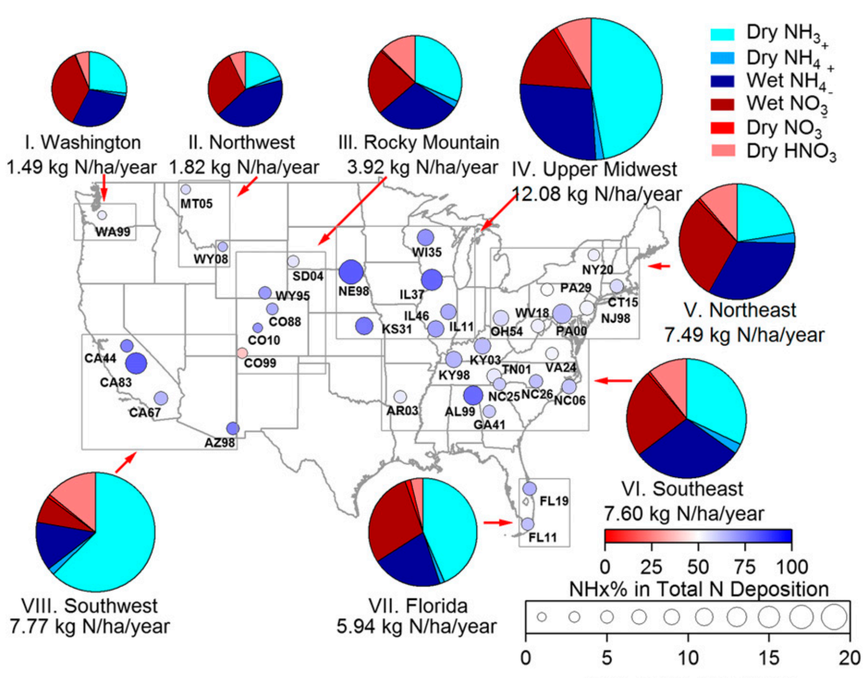

Fig. 5. Spatial trends in total reactive inorganic N deposition across the United States from July 2011 to June 2013. Fractional reduced N contributions to total N deposition (dry + wet) at the 37 sites are represented by circle color. The total inorganic nitrogen deposition is indicated by circle size. The pie charts show average fractional contributions of individual reduced and oxidized N deposition pathways for the eight regions, with each pie area proportional to the average total inorganic nitrogen deposition (also listed under each pie).

than the wet fraction, a point that should be considered in the interpretation of our results.

Fractional Reduced N Contributions to the Total Inorganic N Deposition Budget. With wet and dry deposition estimates available for 37 locations, the total wet plus dry nitrogen deposition budgets can be estimated across the United States (Fig. 5). Fractional deposition contributions by each wet and dry deposition pathway for each of the eight regions are also illustrated in Fig. 5. Reduced N deposition fractions in the eight regions range from 58% (Washington, I) to 78% (Southwest, VIII), with dry NH_3 deposition alone contributing between 19% (Northwest, II) and 63% (Southwest, VIII). Fractional reduced N contributions at individual sites range from 42% at CO99 (Mesa Verde National Park) to 84% at CA83 in California's Central Valley. Ammonia dry deposition fractions ranged from 11% (PA27) to 74% (CA83). The spatial patterns of reduced N deposition fraction generally reflect spatial variations in agricultural activity including animal husbandry. Assuming that the biases between the MLM deposition velocity and bidirectional flux approaches shown in Fig. 4 are generally representative, a full assessment using the bidirectional approach would, at many sites, reduce overall deposition rates and the relative fraction of NH_3 dry deposition. However, the general pattern observed in Fig. 5 remains consistent; NH_x still contributes the majority of inorganic N deposition at the national scale.

The site-specific circle sizes in Fig. 5 indicate the combined wet plus dry inorganic N deposition fluxes. Some regions exhibit majority dry deposition [e.g., dry deposition contributions of 58% and 79% in the Upper Midwest (IV) and Southwest (VIII), respectively], whereas others are more strongly influenced by wet deposition [e.g., wet deposition contributions of 66% and 72% in the Washington (I) and Southeast (VI) regions, respectively]. The largest deposition fluxes at individual sites tend to be observed at locations where fractional reduced N contributions are large. The maximum regional average inorganic N deposition flux (12.1 kg N/ha per year) was observed in the Upper Midwest region (IV); relatively large deposition fluxes were also observed for California and the eastern United States. These spatial patterns are similar to those identified in recent model simulations (43).

Implications and Summary. Increases in agricultural emissions of ammonia and the success of regulatory policies in decreasing NO_x emissions over the last two decades are changing the face of US reactive nitrogen deposition. Although US wet inorganic N deposition was once dominated by nitrate, wet inorganic N deposition now comes mostly from ammonium at nearly 70% of US monitoring sites. Although estimates of dry deposition fluxes of inorganic N inherently contain more uncertainty, dry and total (wet plus dry) inorganic N deposition fluxes also appear to be dominated by reduced N in most parts of the country. Decreases in wet and dry deposition fluxes of oxidized inorganic N species are expected to continue into the future as the United States continues to lower NO_x emissions. Current projections of ammonia emissions growth, meanwhile, suggest that reduced N deposition levels will grow in the future. In addition to the adverse impacts of reduced N deposition on ecosystem health, ammonia is an important precursor to fine particle formation. Fine particles decrease visibility (44) and negatively impact human health and increase health care costs (45, 46). Reductions in US ammonia emissions from agricultural and nonagricultural sources, whether by regulation or voluntary actions (e.g., agricultural producer adoption of best management practices), would yield a variety of positive benefits for ecosystems and society. Increased study of atmospheric ammonia concentrations and improved measures of ammonia dry deposition fluxes are needed to design optimal strategies for achieving such benefits.

Methods

Weekly precipitation concentrations of NH_4^+ and NO_3^- were obtained from the NADP National Trends Network (NTN; 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; https://www.epa.gov/castnet). Biweekly concentrations of gaseous NH_3 were taken from the NADP AMoN (nadp.isws.illinois.edu/AMoN/). To gain greater spatial coverage of airborne NH_3 concentrations, especially in the western United States, NH_x (NH_3 + NH_4^+) measurements from a pilot IMPROVE NH_x monitoring network (28) were also used. More detailed information about these observation networks can be found in Table S2.

Wet deposition data were obtained from NTN sites for the periods 1990–1992 and 2010–2012. The number of sites analyzed changed due to network development over this period. From 1990 to 1992, there were 195 sites; 238 sites were available for the 2010–2012 period. Sites were not included if data were unavailable for ≥1 y in either period examined.

Oxidized and reduced N gas and particle concentrations were obtained for 37 sites (Table S1) where NTN and CASTNET monitoring stations were collocated with AMoN and/or IMPROVE NH_x sites. At 30 of these locations, 2 y of measurements (July 2011 to June 2013) were available. The remaining sites had data availability of at least 1 y. Concentrations of all species that contribute to the N_r deposition budget are not measured at these sites. Important missing compounds include inorganic (e.g., NO_2) and organic N (e.g., alkyl nitrates, peroxyacetyl nitrate, and amines) species. Wet deposition of organic N is also not routinely measured and therefore not considered in this analysis.

Wet N deposition was determined from the amount of total precipitation and the aqueous concentrations of NH_4^+ and NO_3^-. Dry N deposition was calculated for each species as the product of the N species concentration and a 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 on the MLM (47), with input of on-site meteorology and local site characteristics. Gaps in the meteorological data were addressed by using the CASTNET substitution method (48). The deposition velocity of NH_3 is difficult to determine due to the bidirectional nature of the dry NH_3 flux that depends strongly on local conditions (40). To estimate dry NH_3 deposition here, its deposition velocity was calculated as 70% of the HNO_3 deposition velocity following previous estimates (49–51). A review of field observations suggests that the NH_3 deposition velocity is at least half and perhaps as high as the HNO_3 deposition velocity. Our choice of 70% agrees well with the findings of Neirynck et al. (52) and Nemitz et al. (39).

This NH_3 deposition velocity approach is a simple approximation of unidirectional air-surface exchange, ignoring important bidirectional exchange processes that influence the magnitude and direction of the flux. To assess the potential importance of these bidirectional exchange processes and their impact on annual reactive N deposition budgets, NH_3 fluxes derived from the unidirectional approach were compared with fluxes estimated using a two-layer bidirectional flux model (53). The bidirectional model uses hourly CASTNET meteorology and 2-wk integrated AMoN 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. (40) for natural vegetation. Development of this modeling framework is ongoing. Thus, the comparison is constrained to the dominant natural vegetation type at each site for which the Massad et al. (40) parameterizations are applicable, which excludes fertilized and nitrogen fixing crops and some other surfaces specified by CASTNET, including water, sand, and rock. Details of the bidirectional model and comparison are included in *SI Methods*.

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