



Toward the improvement of total nitrogen deposition budgets in the United States

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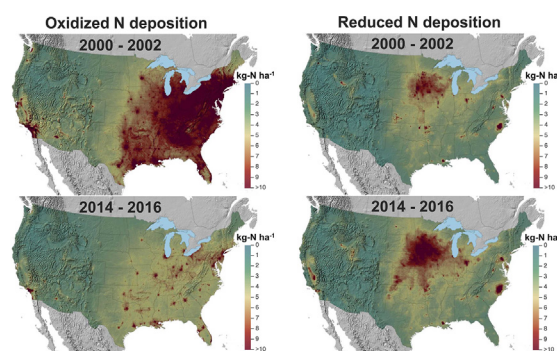
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HIGHLIGHTS

- Deposition budgets for inorganic nitrogen have improved over the last decade in the U.S.
- Important data and knowledge gaps in monitoring and modeling of total nitrogen deposition remain.
- Expanded monitoring of deposition in agricultural and urban areas is needed.
- Monitoring of organic N deposition and improvement of organic N in atmospheric models is needed.
- Land use specific modeled deposition estimates are needed for critical load assessments.

GRAPHICAL ABSTRACT



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ABSTRACT

Frameworks for limiting ecosystem exposure to excess nutrients and acidity require accurate and complete deposition budgets of reactive nitrogen (Nr). While much progress has been made in developing total Nr deposition budgets for the U.S., current budgets remain limited by key data and knowledge gaps. Analysis of National Atmospheric Deposition Program Total Deposition (NADP/Total Deposition) data illustrates several aspects of current Nr deposition that motivate additional research. Averaged across the continental U.S., dry deposition contributes slightly more (55%) to total deposition than wet deposition and is the dominant process (>90%) over broad areas of the Southwest and other arid regions of the West. Lack of dry deposition measurements imposes a reliance on models, resulting in a much higher degree of uncertainty relative to wet deposition which is routinely measured. As nitrogen oxide (NO_x) emissions continue to decline, reduced forms of inorganic nitrogen (NH_x = NH₃ + NH₄⁺) now contribute >50% of total Nr deposition over large areas of the U.S. Expanded monitoring and additional process-level research are needed to better understand NH_x deposition, its contribution to total Nr deposition budgets, and the processes by which reduced N deposits to ecosystems. Urban and suburban areas are hotspots where routine monitoring of oxidized and reduced Nr deposition is needed. Finally, deposition budgets have incomplete information about the speciation of atmospheric nitrogen; monitoring networks do not capture important forms of Nr such as organic nitrogen. Building on these themes, we detail the state of the science of Nr deposition budgets in the U.S. and highlight research priorities to improve deposition budgets in terms of monitoring and flux measurements, leaf- to regional-scale modeling, source apportionment, and characterization of deposition trends and patterns.

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1. Background

Over the past two decades, interest in atmospheric inputs of reactive nitrogen (Nr) to terrestrial and aquatic ecosystems has increased dramatically within the U.S. National Atmospheric Deposition Program (NADP) user community. Nr refers to all biologically active, chemically reactive, and photochemically active nitrogen compounds. Nitrogen deposition refers to the transfer of nitrogen-containing compounds from the atmosphere to the Earth's surface. Atmospheric inputs occur via wet deposition processes through which gases or aerosols are first incorporated into hydrometeors and then delivered to the surface through precipitation, or by dry deposition processes through which gases or particles are deposited to surfaces directly. Wet and dry deposition processes considered together represent "total" nitrogen deposition.

Nitrogen deposition is an important step in the nitrogen cascade concept, which describes the cycling of Nr between the atmosphere and biosphere (Galloway et al., 2003). The amount of Nr in the environment has doubled globally over the past century (Fowler et al., 2013) with large recent increases occurring in developing countries (Huang et al., 2017; Amann et al., 2013) owing largely to anthropogenic processes including fertilizer use and fossil fuel combustion. Impacts of excess Nr include soil and lake acidification, changes in terrestrial

biodiversity, drinking water contamination, and reduced resilience of ecosystems to climate variability and other stressors (EPA, 2008; Bobbink et al., 2010; Wright et al., 2018). Excess Nr deposition can degrade the quality of benefits provided by ecosystems, including clean water, climate regulation, food, recreational opportunities, and cultural and spiritual value (Compton et al., 2011; Cooter et al., 2013; Munns Jr. et al., 2016a). The recognition that the atmosphere plays a key role in providing these services (Cooter et al., 2013; Rea et al., 2012; Thornes et al., 2010) has underscored the need to develop accurate and complete atmospheric Nr deposition budgets.

1.1. U.S. air regulations relevant to Nr

The National Ambient Air Quality Standards (NAAQS), established under the Clean Air Act (CAA), include primary standards to protect public health and secondary standards to protect public welfare. The CAA definition of "welfare" includes effects on soils, water, vegetation, visibility, weather, climate, wildlife, materials, economic values, and personal comfort and well-being. The secondary NAAQS are based on air concentration rather than rates of deposition. The secondary standard for nitrogen dioxide (NO₂), which establishes a limit of 0.053 ppm annual average concentration, is the standard most directly relevant to Nr deposition. In addition to establishing the standards

themselves, the CAA requires periodic review and, as necessary, revision of the NAAQS. Central to the NAAQS review process is the Integrated Science Assessment (ISA), which is a comprehensive synthesis and evaluation of the most policy-relevant science related to the standard. Due to their combined effects on atmospheric chemistry, deposition processes, ecosystem health, and public welfare, the secondary standards for NO₂ and sulfur dioxide (SO₂) (0.5 ppm 3-hour average air concentration) were most recently reviewed together (Final Rule, U.S. EPA, 2012), referred to here as the Integrated Science Assessment for Oxides of Nitrogen (NO_x) and Sulfur (SO_x) or NO_x/SO_x ISA (U.S. EPA, 2008). In the current ongoing review, PM is also included (U.S. EPA, 2017). While the standard is based on air concentrations, the NO_x/SO_x review encompasses ecosystem effects resulting from direct exposure to atmospheric concentrations, as well as atmospheric deposition, understanding that deposition rates are fundamentally linked to atmospheric concentrations.

The scope of the secondary NAAQS review is not limited to the specific indicators of the current standards, that is, NO₂ and SO₂. The most recently completed NO_x/SO_x ISA (U.S. EPA, 2008) acknowledges that comprehensive assessment of the ecological effects of atmospheric N_r deposition requires consideration of the suite of chemical forms that make up N_r. The ISA therefore evaluates data on all oxidized, reduced (ammonia (NH₃) and ammonium (NH₄⁺), NH_x = NH₃ + NH₄⁺), and organic forms of nitrogen in atmospheric deposition. The 2008 NO_x/SO_x ISA concluded that evidence is sufficient to infer a causal relationship between deposition of acidifying species and effects on biota and biogeochemistry related to terrestrial and aquatic ecosystems (U.S. EPA, 2008). The review further determined that known or anticipated adverse ecological effects are occurring and that the current standards are not adequate to protect against deposition-related effects (U.S. EPA, 2009, 2011a). An independent advisory committee concluded that the levels and the form of the current standard are insufficient to protect against adverse effects from deposition, thus warranting revision of the standard (U.S. EPA, 2011b). Ultimately the standard was not revised due to uncertainty related to setting the form, indicator, and level of the standard (U.S. EPA, 2011b). Current research continues to investigate the use of metrics such as the transference ratio to more directly link atmospheric concentrations to ecosystem exposures to support implementation of the secondary NAAQS (Scheffe et al., 2014; Sickles and Shadwick, 2013; Sickles et al., 2013; Koo et al., 2015).

N_r plays an important role in other air quality regulations, including the primary NAAQS and the Regional Haze Rule. The primary NAAQS set air concentration limits for several pollutants that are known to be harmful to human health, including NO₂, ozone (O₃), and particulate matter (PM). Atmospheric N_r directly contributes to both the formation of O₃ and PM (Galloway et al., 2003; Fowler et al., 2013). Oxidized nitrogen gases are primary precursors of O₃ formation and are important in O₃ control strategies. N_r reacts with organic carbon compounds leading to secondary organic aerosol (SOA) and both reduced and oxidized forms of N_r play a role in the formation of inorganic PM, specifically NH₄⁺ containing compounds, and contribute significantly to the total mass of PM in the atmosphere (Ng et al., 2017; Hand et al., 2012). Atmospheric PM is not only a concern for human health but also for its effects on climate and atmospheric visibility. Visibility is a protected resource in some large national parks and wilderness areas, collectively called Class I areas, where scenic views are a valued ecosystem service. The CAA established the goal of reducing haze to natural levels in these areas and the Regional Haze Rule, enacted in 1999, calls for states to establish emission reduction programs to achieve this goal (U.S. EPA, 1999).

1.2. Critical loads of nutrients and acidity

A fundamental aspect of characterizing ecosystem risk from nutrient enrichment or acidification is quantifying the amount of N_r entering the ecosystem that leads to a measurable shift in an ecosystem process. A

critical load is defined as “a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge” (Nilsson and Grennfelt, 1988). The critical load exceedance is the difference between the total amount of deposition and the critical load. Critical loads are calculated by measuring or modeling shifts in ecosystem function with increasing levels of deposition. Thus, development of critical load frameworks for N_r requires an accurate assessment of the total amount of N_r in atmospheric deposition. Critical loads linking atmospheric deposition to ecological response have been developed for a number of ecosystem impacts in North America including terrestrial and aquatic acidification, forest-tree and forest-soil health, nitrate (NO₃⁻) leaching, changes in plant community composition, and changes in lichen communities (Clark et al., 2018).

In 2004, the National Research Council (NRC) recommended that EPA consider using critical loads for ecosystem protection, which was followed in 2005 by an EPA rule that includes a provision for states to use critical loads as part of their air quality management strategy to satisfy CAA requirements regarding “prevention of significant deterioration” (PSD) (U.S. EPA, 2005). PSD addresses the preservation, protection, and enhancement of air quality and air quality related values (e.g., ecosystem services) in national parks, national wilderness areas, national monuments, national seashores, and other areas of special national or regional natural, recreational, scenic, or historic value (U.S. Congress, 1977). The 2004 recommendation by the NRC and 2005 EPA ruling were followed by an expansion of critical loads research. Critical loads are now used by EPA as a quantitative framework for linking deposition to effects on public welfare and thus have become an important assessment tool within the secondary NAAQS review process (Scheffe et al., 2014; Rea et al., 2012). Additionally, U.S. federal land management agencies have adopted critical loads as a tool for setting management goals and guiding air pollution management decisions for national parks, forests, and wilderness areas (Blett et al., 2014; Pardo et al., 2015). Establishment of a critical load for eutrophication in Rocky Mountain National Park (RMNP) (Baron, 2006; Porter and Johnson, 2007) and the Rocky Mountain National Park Nitrogen Deposition Reduction Plan (CDPHE, 2007) are examples of federal agencies (U.S. EPA, Region 8; National Park Service (NPS)) and states (Colorado Department of Public Health and Environment) working collaboratively to develop and implement an air quality management plan to protect public welfare and ecosystem services by reducing rates of N_r deposition.

While critical loads are often identified for the most sensitive components within an ecosystem, they can be linked to public welfare by connecting the ecological consequence to ecosystem services that benefit people (Munns Jr et al., 2015). An assessment of 47 terrestrial and aquatic critical load exceedances indicate a relationship with over 1000 ecosystem goods and services (Bell et al., 2017). For example, when a critical load for acid neutralizing capacity is exceeded in lakes and streams, it can be linked to changes in recreational fish species abundance, which impacts ecosystem services such as recreational use by anglers or cultural and spiritual values (Rea et al., 2012; O'Dea et al., 2017). By linking atmospheric deposition to ecosystem response in the context of ecosystem services, critical loads provide a quantitative framework that can be used to inform resource management and policy decisions aimed at sustaining or improving human welfare (Munns Jr. et al., 2016b). For managers and policy makers to feel comfortable using these relationships, it is necessary to understand the certainty of the critical load exceedance.

Critical loads have been used extensively in Europe to support the Convention on Long-range Transboundary Air Pollution (LRTAP) within the UN Economic Commission for Europe (UNECE). Maps of critical levels and loads are regularly updated within the LRTAP Working Group on Effects lead by the International Cooperative Programme on Modeling and Mapping of Critical Levels and Loads and Air Pollution Effects, Risks and Trends (<http://icpmapping.org/>). Maps of critical load

exceedances support pollutant emission reduction strategies developed under the UNECE Convention on LRTAP (UNECE, 2004). In North America, critical loads have also been used in Canada to design emission reduction programs (Jeffries and Ouimet, 2004) and in reporting under the U.S.-Canada Air Quality Agreement. In Mexico, federal regulations exist for emissions of NO_x and ambient concentrations of NO_2 , but critical loads have thus far not been adopted for ecosystem protection.

Accurate and complete deposition budgets of nutrients and acidity are fundamental requirements for the development of critical loads and protection of human welfare. While much progress has been made in developing total deposition budgets for the U.S. over the past several years, improvement in the completeness, accuracy, and spatial representativeness of total N_r deposition budgets remains limited by key data and knowledge gaps. We present here an overview of the current state of the science of total N_r deposition budgets in the U.S. using the NADP Total Deposition (TDep) measurement-model fusion (MMF) product (<http://nadp.slh.wisc.edu/committees/tdep/tdepmaps/>). We use this brief illustration of current trends and patterns in N_r deposition (Section 2) to motivate a more detailed discussion of the current science in Section 3. The science topics are not intended to be comprehensive, and were selected by deliberation within the NADP TDep science committee based on prioritization of needs, feasibility of progress, and relevance to the larger field of deposition science. The topics are organized by: (1) measurement of deposition, further categorized as “routine monitoring”, including measurements potentially deployable in a monitoring network, and “non-routine” or measurements collected in a more intensive mode typically to characterize process level phenomena; (2) modeling of deposition budgets; (3) MMF techniques, (4) source apportionment, and (5) characterization of uncertainty in deposition measurements and estimates. Section 4 presents examples of overarching research themes that emerge from the key knowledge and data gaps discussed in Section 3 where enhanced coordination across stakeholder groups is needed to advance deposition science more rapidly. For more detailed descriptions of the science topics described here, the reader is referred to the recent NADP/TDep report on the subject (<http://nadp.slh.wisc.edu/committees/tdep/reports/nrDepWhitePaper.aspx>; Walker et al., 2019a).

2. Current patterns and trends in N_r deposition in the U.S.

Determination of the amount of deposition to ecosystems in excess of the critical load (i.e. exceedance) requires an estimate of total deposition, which may be derived from deposition measurements, site-specific inferential models, gridded chemical transport models (CTMs), or a combination of measurements and CTM output (i.e., MMF). Information on North American pollutant monitoring networks can be found in Appendix A (Table A1). Gridded deposition maps developed using the TDep MMF approach (Schwede and Lear, 2014) are commonly used for critical loads assessments in the U.S. The TDep MMF procedure combines spatially interpolated air concentrations from the Clean Air Status and Trends Network (CASTNET) with deposition velocities from the Community Multi-scale Air Quality Model (CMAQ V5.0.2) to produce ‘measured’ dry deposition grids for measured species (i.e. gas phase nitric acid (HNO_3) and particulate NO_3^- and NH_4^+). CMAQ dry deposition values are then bias adjusted with CASTNET measurements and combined with the measured dry deposition grids. The bias adjustment is done to remove any step-functions between the measured and modeled values as these are transitioned with distance from the monitoring site using an inverse distance weighting (IDW) function. For species not measured routinely at CASTNET sites (i.e. gas phase nitric oxide (NO), NO_2 , nitrous acid (HONO), dinitrogen pentoxide (N_2O_5), NH_3 , peroxyacyl nitrates (PANs), and organic nitrates), the CMAQ dry deposition values are used directly. Dry deposition for the measured and unmeasured species is combined to quantify total N dry deposition. Dry deposition is combined with

measured and spatially interpolated wet deposition values from the NADP’s National Trends Network (NADP/NTN) and Atmospheric Integrated Research Monitoring Network (NADP/AIRMon) to produce values of total deposition of N for the continental U.S. (CONUS) on a 4×4 km grid resolution. More detailed information is available from <http://nadp.slh.wisc.edu/committees/tdep/tdepmaps/>.

Fig. 1 summarizes several important features of total N_r deposition patterns using the most recent total deposition maps derived from the TDep MMF procedure (Schwede and Lear, 2014; NADP, 2018) averaged over the period 2014–2016. Across the CONUS, total deposition (Fig. 1A) ranges from 0.7 to 71.0 kg N ha⁻¹ yr⁻¹, with 50% of total deposition rates within the range of 3.7 to 9.2 kg N ha⁻¹ yr⁻¹. Mean and median deposition rates are equivalent at 6.7 kg N ha⁻¹ yr⁻¹. Lowest deposition rates (<2.0 kg N ha⁻¹ yr⁻¹) occur in more remote areas of the West and Southwest, while highest deposition rates (>15 kg N ha⁻¹ yr⁻¹) occur in the Midwest and other agricultural areas (e.g., eastern North Carolina, southeastern Pennsylvania) associated with NH_3 emissions from animal production facilities and fertilized soils. Urban areas such as Los Angeles and New York City also appear as deposition hot spots, reflecting the contribution of NO_2 dry deposition associated with mobile sources of nitrogen oxides (NO_x).

Averaged across the CONUS, dry deposition (Fig. 1B) contributes slightly more (55%) than wet deposition to total deposition and is the dominant process (>90%) in arid regions, particularly the deserts of the Southwest and on the leeward side of western mountain ranges (e.g. the Cascades and Sierra Nevadas). In the East, the largest contributions from dry deposition occur in agricultural areas (e.g., southeastern Pennsylvania, eastern North Carolina, Delmarva peninsula) where NH_3 dry deposition rates are large, and in urban areas (e.g., Orlando, Florida; Atlanta, Georgia; Washington, D.C.; New York City, New York; Boston, Massachusetts) where NO_2 dry deposition associated with mobile NO_x emissions is important. The general lack of dry deposition measurements, which are not conducted in a routine mode like wet deposition, imposes a reliance on models for this component of the deposition budget. This lack of measurement data, coupled with the complexity of the dry deposition processes themselves, results in a much higher degree of uncertainty relative to wet deposition, and follows that in many areas, the most important pathway of ecosystem exposure is also the most uncertain.

An important characteristic of the total deposition budget is the relative contributions of reduced (e.g., NH_3 gas + NH_4^+ aerosol) versus oxidized forms of inorganic N_r to total N_r deposition. Reduced inorganic N_r in the atmosphere primarily originates from agricultural sources of NH_3 , including animal manure and fertilized soil, whereas oxidized inorganic N is primarily emitted from combustion sources. In contrast to NO_x emissions, emissions of NH_3 are not regulated in the U.S. Recent studies (Li et al., 2016; Zhang et al., 2018a) show that the relative contribution of reduced forms of nitrogen to the atmospheric inorganic nitrogen budget is increasing over time. These trends are reflected in Fig. 2, which summarizes TDep maps of oxidized and reduced N deposition (wet + dry deposition) averaged over the periods 2000 to 2002 and 2014 to 2016. Fig. 1C shows that reduced forms of inorganic nitrogen now contribute >50% of total N_r deposition over large areas of the CONUS, broadly consistent with spatial patterns of agricultural NH_3 emissions.

The change in the N_r deposition budget between 2000 and 2016 is a result of a ~50% reduction in U.S. NO_x emissions (U.S. EPA, 2018). Relative to NO_x sources, NH_3 emissions are more spatially and temporally variable, thus making regional and national trends in NH_3 emissions more difficult to quantify using emission factors and county-level agricultural activity data (Butler et al., 2016; Xing et al., 2013). However, ground based (Butler et al., 2016; Saylor et al., 2015) and satellite observations (Warner et al., 2017) indicate increasing NH_3 air concentrations in some areas of the U.S., consistent with increasing trends in measured wet deposition of NH_4^+ (Du et al., 2014; Li et al., 2016).

As the relative contribution of the reduced component of the N_r deposition budget is increasing, knowledge of the spatial and temporal

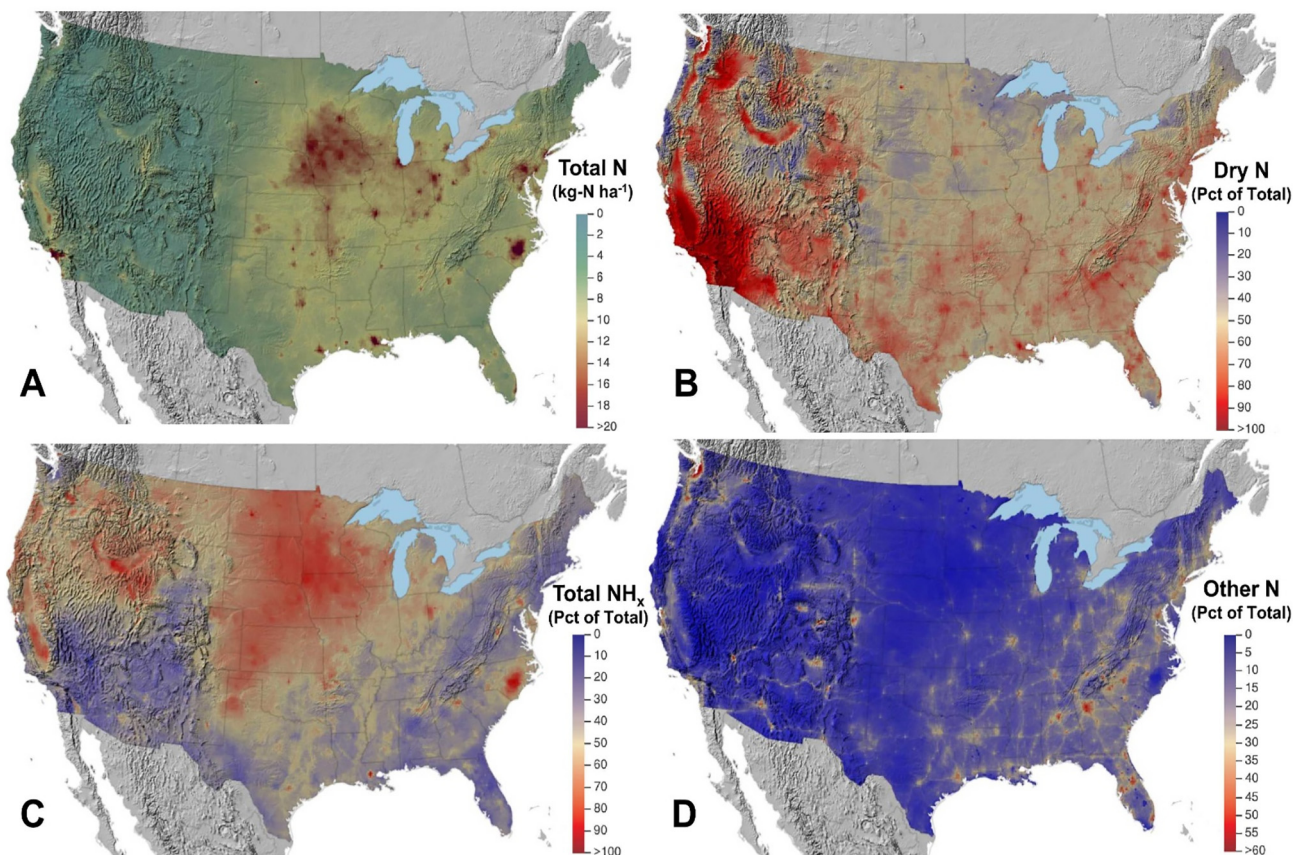


Fig. 1. Summary of TDep maps (NADP, 2018) for the continental U.S., averaged over the period 2014–2016, of (A) total N deposition, (B) percentage of total N deposition attributed to dry deposition, (C) percentage of total deposition attributed to reduced N ($\text{NH}_x = \text{NH}_3 + \text{NH}_4^+$), and (D) percentage of total deposition attributed to dry deposition of unmeasured “Other N” species comprising NO, NO_2 , HONO, N_2O_5 , and organic N.

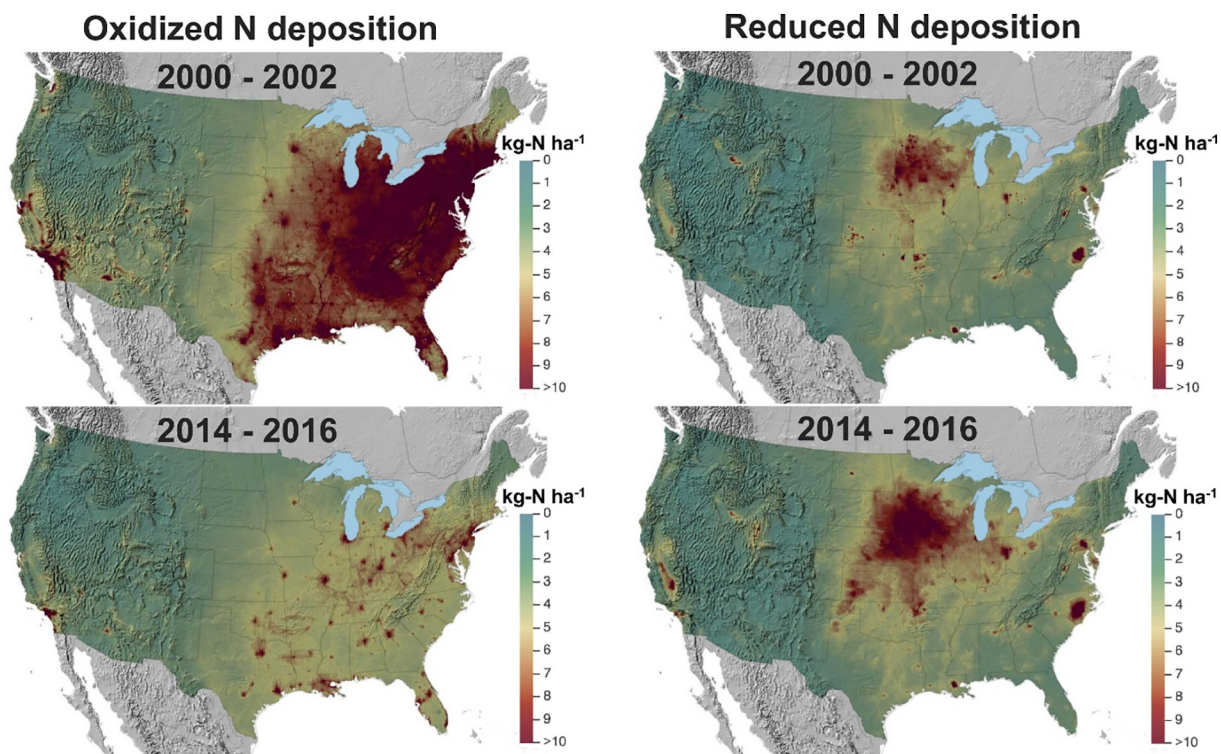


Fig. 2. Summary of TDep maps (NADP, 2018) of total oxidized (left) and reduced ($\text{NH}_3 + \text{NH}_4^+$, right) N deposition averaged over the periods 2000–2002 (top) and 2014–2016 (bottom).

patterns of NH_3 and NH_4^+ deposition is becoming more important for understanding ecological impacts and for developing approaches to maintain or reduce deposition rates below critical N loads. As detailed in the following sections, NH_3 is unique to other Nr compounds in that it is exchanged bi-directionally between surfaces and the atmosphere, making accurate measurements, source apportionment, and model estimates of NH_3 deposition rates challenging. A more complete understanding of the processes by which NH_3 and NH_x deposit to ecosystems and their contributions to total Nr deposition budgets is needed.

Another important aspect of the TDep total deposition budget shown in Fig. 1A relates to overall completeness of the budget. As described in more detail in the following sections, monitoring networks that support U.S. deposition assessments characterize only the inorganic fraction of wet deposition (i.e., NADP/NTN) and atmospheric concentrations of particles and gases (i.e., CASTNET) and are thus incomplete with respect to speciation of the complete atmospheric Nr pool. Several key compounds or groups of compounds are not routinely measured in these networks, yet are known to contribute significantly to Nr deposition budgets. These include organic compounds in the gas and particulate phases and additional inorganic oxidized compounds such as NO_2 . The TDep mapping process for dry deposition relies on CMAQ predictions of air concentrations for oxidized and organic N compounds not monitored by CASTNET, which for CMAQ version 5.0.2 includes NO , NO_2 , HONO , N_2O_5 , and a subset of organic N (ON) comprising peroxyacyl nitrate (PAN), aromatic PANs (OPAN), C3 and higher PANs (PANX), and several other organic nitrates in the gas phase. These species are grouped as unmeasured "Other N" in the TDep process. Relative to components of the budget that are measured directly (i.e. wet NH_4^+ and NO_3^-) or bias corrected in the TDep methodology using measured air concentrations (i.e. dry HNO_3 , NO_3^- , and NH_4^+), the unmeasured dry deposited component derived from CMAQ is much more uncertain.

As shown in Fig. 1D, dry deposition of the "Other N" fraction contributes ~ 13% of total deposition over the CONUS on average, with much larger contributions in urban areas and along major roadways where NO_2 associated with mobile NO_x emissions is important. Urban and suburban areas generally appear as hotspots of deposition for oxidized nitrogen. While NO_x and NO_2 are monitored in some urban and suburban areas (see Appendix A), these data are not currently incorporated into the TDep fusion process. The work of Fenn et al. (2018a) highlights that NH_x deposition in urban areas is likely underestimated in these maps due to underestimation of NH_3 emissions from mobile sources in current inventories (Sun et al., 2017). However, with the exception of a relatively few cities, these environments are not covered by the networks that support deposition research (NTN, AIRMoN, CASTNET), which were designed to characterize rural environments.

Organic forms of N are an important component of atmospheric Nr not measured in U.S. national monitoring networks. The global syntheses of Jickells et al. (2013) and Cape et al. (2011) show that ON compounds contribute ~25% of total water-soluble N in precipitation on average, with a similar contribution in particulate matter. In the U.S., contributions range from ~3% to 33% of total N as ON in precipitation and PM (Scudlark et al., 1998; Keene et al., 2002; Whitall and Paerl, 2001; Beem et al., 2010; Benedict et al., 2013; Walker et al., 2012a; Zhang et al., 2002; Russell et al., 2003; Calderón et al., 2007; Lin et al., 2010; Zamora et al., 2011; Chen et al., 2018). Wet deposition of ON is not measured in the NADP/NTN or AIRMoN networks, and thus not included in the TDep MMF total N deposition budget (Fig. 1A). Due to a lack of routine measurements of ON in precipitation and incomplete treatment of ON dry deposition in CMAQ V5.0.2, total deposition of Nr is underestimated by an unknown but likely significant amount in the TDep maps. This would translate to an overestimation of the contribution of inorganics to total deposition (Fig. 1B, C, and D). It should be noted that improvement of ON representation in CTM chemical mechanisms is an active area of research (Luecken et al., 2019; Pye et al., 2015).

The issues outlined above, and others addressed in the following sections, result in potentially large uncertainties and biases in the

current Nr deposition estimates. Quantifying the uncertainties in the Nr deposition themselves represents a knowledge gap in the utility of the estimates as their magnitude is not known. We refer to this as the 'uncertainty of the uncertainty', but the limitation is significant. The major example of this is the critical load exceedance metric since its uncertainty may be an important consideration in the development and implementation of strategies to address excess Nr deposition. The uncertainty in the exceedance depends on the uncertainty in both the Nr deposition rates and estimation of the critical load threshold and the former is currently unknown. Fig. 3 summarizes exceedance and corresponding total N deposition for critical loads of a decrease in herbaceous richness at sites across the U.S. (Simkin et al., 2016). At approximately 12% ($N = 1860$) of the sites, the total deposition amount is within $\pm 2.0 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ of the critical load. These "near exceedance" locations represent a broad range of Nr deposition levels ($6.0\text{--}16.0 \text{ kg N ha}^{-1} \text{ yr}^{-1}$), demonstrating that uncertainty in determining whether a critical load is exceeded is important at both high and low levels of deposition.

In the following sections, the state of the science of Nr deposition in the U.S. is explored in more detail, focusing on key knowledge and data gaps from the perspective of both measurements and models.

3. Key knowledge and data gaps in specific areas of Nr deposition science

3.1. Measured Nr deposition budgets

Deposition budgets can employ both routine and process-level measurements. Routine monitoring is more of a "top-down approach" to acquire large amounts of concentration and deposition data in a standardized and large-scale approach to characterize patterns and trends. These Nr measurements should be performed relatively easily and at a relatively low cost to understand the patterns of Nr deposition on a regional scale and to evaluate CTMs. Process-level measurements are typically conducted intensively for short duration to understand the physical, chemical, and biological processes of air-surface exchange to improve models and characterize effects.

3.1.1. Routine monitoring

3.1.1.1. Spatial and temporal patterns of atmospheric NH_3 . Approximately 80% of the anthropogenic NH_3 emissions in the U.S. are from agricultural sources, with confined animal feeding operations (CAFOs) accounting for ~55% and fertilized soils accounting for ~25% (U.S. EPA, 2014). The magnitude and dynamic nature of emissions from CAFOs and fertilized soils, along with the dense spatial distribution of CAFOs in some areas, results in large spatial and temporal variability of NH_3 emissions within agricultural regions. This results in high spatio-temporal variability of NH_3 air concentrations in and around agricultural areas of the U.S., which has been observed in ground-based (Li et al., 2017; Puchalski et al., 2016; Walker et al., 2004) and remotely sensed measurements (Pinder et al., 2011; Schiferl et al., 2016; Warner et al., 2017).

Better characterization of the spatial variability of atmospheric NH_3 concentrations in agricultural areas is needed for improvement of emission inventories and further development and evaluation of CTMs, which will in turn benefit the TDep MMF methodology (Schwede and Lear, 2014). Currently, the TDep process relies solely on CMAQ for estimates of NH_3 dry deposition, which is modeled using a bi-directional flux framework. Ambient NH_3 data from the NADP Ammonia Monitoring Network (AMoN), currently the only national monitoring effort for NH_3 in the U.S., are not used in the TDep process. This is partly due to a lack of understanding of the spatial variability of NH_3 concentrations in agricultural regions and the "radius of influence" for a monitoring location as described by Schwede and Lear (2014). Expanded monitoring to characterize spatial variability in agricultural areas is needed to continue developing a methodology for incorporation of NH_3 monitoring data into the TDep mapping process.

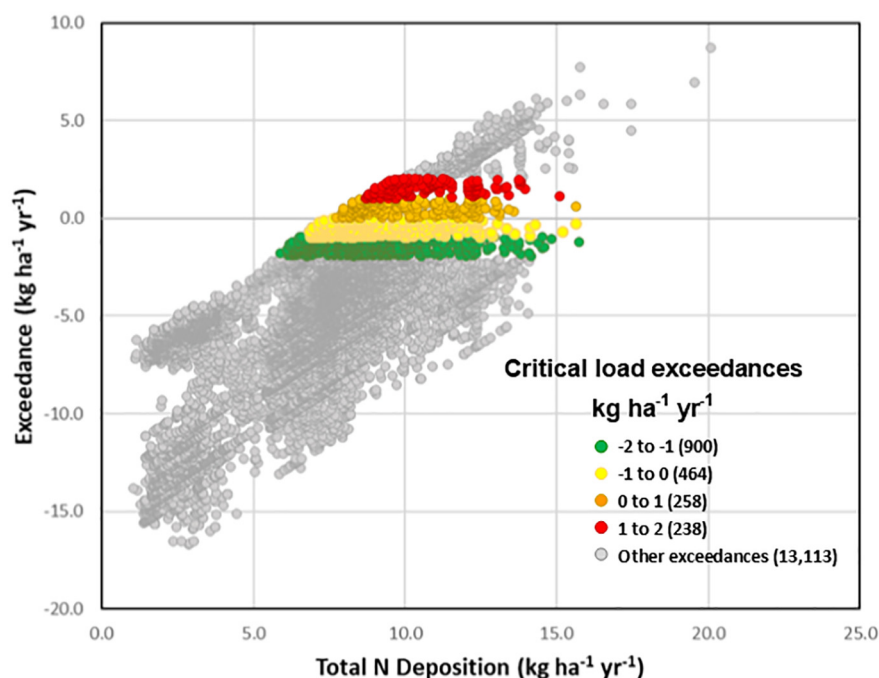


Fig. 3. Exceedance of herbaceous richness critical load based on TDep total N deposition 2013–2015. Negative values of exceedance indicate that the total deposition is less than the critical load. Exceedance data from Simkin et al. (2016). Figure from Walker et al. (2019b).

Fig. 4 shows the current distribution of AMoN sites across the U.S. in relation to county-scale NH_3 emissions from the U.S. EPA, 2014 (V2) National Emissions Inventory. A large number of sites are located in the eastern U.S. in counties with relatively low emissions and there are large geographical areas in agricultural regions where monitors do not currently exist.

Expansion of the AMoN network in agricultural areas in the Midwest and western U.S. is a high priority. In combination with information on emissions, design of this expanded monitoring could be guided by

satellite NH_3 measurements to identify gradients in air concentrations where monitoring is currently sparse or non-existent and to consider spatial variability not evident in current emission inventories. While emissions inventories are developed on a county basis, there can be high spatial variability in emissions within a county. The map of Sampson County, NC (Fig. 4) highlights the complexity of selecting “representative” monitoring sites in agricultural areas and emphasizes the need to consider a number of factors so that monitoring data can be properly interpreted in the context of local versus aggregate larger-

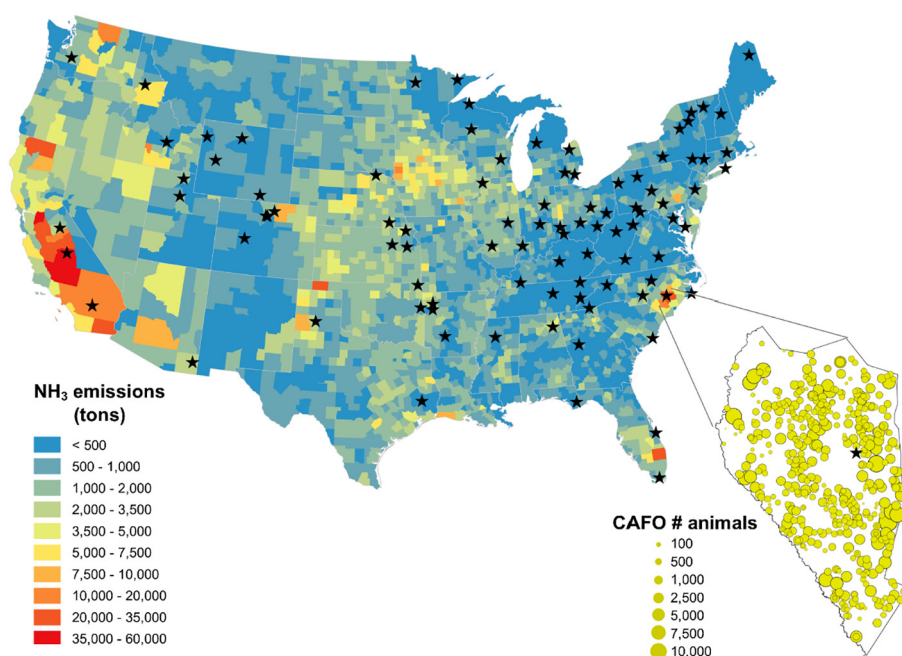


Fig. 4. Map of AMoN NH_3 monitoring sites (stars) and county-scale NH_3 emissions (all categories) from the U.S. EPA, 2014 (V2) National Emissions Inventory (U.S. EPA, 2014). Exploded view of Sampson County, NC showing locations of animal production facilities (NC DEQ, 2019) categorized by # of animals (circles) with location of AMoN site NC35 shown (star).

scale emissions and appropriately compared to gridded atmospheric models. Elements of site selection would include NH_3 emission density of the surrounding area, types of emissions and facilities, and distance from the nearest source.

Given the existing AMoN infrastructure, this monitoring need could be pursued in the near term with modest resources. There is also a need for (1) spatial gradient studies near agricultural sources to characterize concentrations and deposition as a function of distance to the nearest source or sources; and (2) highly time-resolved ambient NH_3 concentration measurements to characterize short-term variations and diurnal patterns for model evaluation.

In addition to expanded monitoring in agricultural areas, a study conducted by Fenn et al. (2018a) illustrates the importance of mobile emissions as a source of NH_3 deposition in urban areas. While agricultural NH_3 emissions dominate the national emission inventory, mobile emissions are likely underestimated (Sun et al., 2017) in current inventories, which is particularly important for modeling N_r budgets in urban and suburban environments. Routine monitoring of NH_3 in urban areas and along urban to rural gradients would be helpful in better understanding the relative portions of oxidized versus reduced forms of N_r deposition in these environments and for evaluating model derived deposition estimates.

3.1.1.2. Routine monitoring of N_r dry deposition. Dry N_r deposition is the primary deposition pathway in many areas of the U.S., especially in arid regions such as the desert Southwest and on the leeward side of western mountain ranges (Fig. 1B). Long term measurements of speciated N_r dry deposition are needed to reduce uncertainty in total deposition budgets, characterize temporal and spatial patterns of dry deposition at regional to national scales, and to evaluate dry deposition models over the full range of atmospheric and surface characteristics that influence seasonal and annual deposition budgets. Time-resolved micrometeorological fluxes are ideal for examining processes but datasets are often limited in temporal extent (days to several weeks) due to cost, technical challenges, logistical constraints, and time needed for processing of complex flux datasets. A dry deposition measurement system suitable for routine deployment within existing infrastructure (e.g., CASTNET, NADP, Canadian Air and Precipitation Monitoring Network (CAPMoN)) is needed. System requirements include low cost, ability to measure the primary components of the inorganic N_r budget, unattended operation, and adherence to micrometeorological flux measurement principles.

Conditional time-averaged gradient (COTAG) approaches (Famulari et al., 2010) satisfy the above requirements. The basic principle employs the aerodynamic gradient approach to calculate air-surface exchange rates from vertical gradients of air concentration integrated over one week to one month. To avoid biases in time integrated gradients associated with diurnal patterns in atmospheric stability, gradients are “conditionally” sampled only during periods that satisfy the micrometeorological requirements of the gradient approach. Variants of the original design of Famulari et al. (2010) were deployed in multiple locations during the NitroEurope project as part of an effort to develop a European network for N_r fluxes, several of which remain in operation (Marsailidh Twigg, CEH, personal communication). These systems employ a low cost, low flow (0.4 Lpm) denuder and filter pack system (DELTA system, Tang et al., 2009) to measure monthly time-integrated concentrations of NH_3 , NH_4^+ , HNO_3 , NO_3^- , SO_2 , sulfate SO_4^{2-} , hydrochloric acid HCl, chloride Cl^- , and base cations. Fluxes are therefore calculated for monthly periods. Evaluation of the systems deployed in Europe is ongoing and has to date focused primarily on SO_2 (Famulari et al., 2010) and NH_3 (Marsailidh Twigg, CEH, personal communication).

Application of this method in the U.S. would require further evaluation of the COTAG approach under representative meteorology, atmospheric chemistry and surface characteristics. Several aspects of system performance, flux uncertainty and suitability of the method for specific sites can be assessed in the short term using existing datasets

such as turbulence and heat flux data from the Ameriflux network (<https://ameriflux.lbl.gov/>) and concentration data from the CASTNET and AMoN networks. Expansion of the established time-integrated denuder/filter pack sampling methods beyond HNO_3 , NH_3 , NO_3^- , and NH_4^+ to include other gas phase N_r species and organic particulate species could also be explored in the near term. Longer-term research efforts would include evaluation of the method over tall vegetation and direct comparison to traditional higher time resolution micrometeorological methods. Deployment of the system at select sites within existing North American monitoring infrastructure is also a longer-term goal.

3.1.1.3. Routine monitoring of organic N. N_r deposition budgets developed from current routine monitoring networks do not fully account for the contribution of organic N forms. The most expeditious approach to establishing routine monitoring of ON in North America is to utilize existing infrastructure for “bulk” measurements in precipitation (NADP/NTN, NADP/AIRMoN, CAPMoN) and PM (CASTNET, CAPMoN). Measurement of bulk ON in precipitation or PM is accomplished by measuring the total concentration of nitrogen and then subtracting the concentrations of the inorganic components (NH_4^+ , NO_3^- , and nitrite (NO_2^-)). While suitable analytical methods for bulk ON are well established (see Walker et al., 2012a and references therein), incorporation of bulk ON measurements into NADP and CAPMoN precipitation networks will require additional work to characterize ON stability and biases associated with field sampling and laboratory methods.

ON may be lost from field samples due to biological conversion or volatility (Cape et al., 2001), or due to interactions with the collector material itself (Scudlark et al., 1998). As shown by Walker et al. (2012a), significantly less ON was measured in weekly NTN samples collected with the standard HDPE bucket compared to daily samples collected in borosilicate glass and refrigerated in-situ. The cause of this bias, i.e., collector material versus stability, was not determined. A next step in identifying the most suitable collection material and establishing a standard protocol would be to compare the NTN bucket, glass sample train, and the bag-type collectors used by CAPMoN. This could be accomplished in a replicated experiment under controlled conditions by splitting a composite sample among the collector types.

A second step is to characterize the stability of ON over time after field collection. Stability can be maintained by in-situ refrigeration (Keene et al., 2002) or use of a chemical preservative (Cape et al., 2001). Both approaches create challenges for NADP and CAPMoN: in-situ refrigeration would require modification of existing collectors while use of a chemical preservative may be incompatible with current analytical protocols. From a cost standpoint, use of a chemical preservative, rather than refrigeration, may be more feasible for network wide implementation. Identification of a suitable preservative would first require testing for compatibility with existing methods followed by field testing at several sites representing a range of atmospheric chemical conditions and ambient temperatures. Should the use of a preservative prove unfeasible, a modified collector, in which the sample is refrigerated in-situ and shielded from sunlight, could be deployed at a subset of sites to maintain the weekly sampling schedule. This may be more economically feasible for NTN than implementing daily sampling at a subset of sites.

For PM measurements conducted under CASTNET and CAPMoN, the analytical method for total N developed for NTN (Walker et al., 2012a) could be applied to provide weekly (CASTNET) and daily (CAPMoN) measurements of bulk water-soluble ON in aerosols. While measurements of total N, and therefore bulk ON, could be implemented rather easily, additional field testing would be needed to assess issues of organic N stability in the field, particularly for weekly CASTNET samples. This would involve comparison of weekly integrated samples to averages of shorter-term measurements (i.e., daily). Testing will be needed to identify suitable methods for capture of volatile species liberated from the aerosol phases, analogous to the use of a backup nylon filter

to capture HNO_3 from volatilized NH_4NO_3 , and to characterize other processes, such as hydrolysis (Rindelaub et al., 2016; Boyd et al., 2015) affecting organic PM on the filter in the field and during storage after extraction.

3.1.1.4. Urban deposition. Over 50% of the world's population lives in urban areas with an expected increase to 66% by 2050 (United Nations, 2015). Owing to the density of emissions from stationary and mobile sources in population centers, urban-to-rural transect studies conducted in North America (e.g., Los Angeles (Bytnerowicz et al., 2015; Padgett et al., 1999; Fenn et al., 2018a), New York (Lovett et al., 2000), Boston (Templer and McCann, 2010; Rao et al., 2014), Baltimore County (Bettez and Groffman, 2013), Phoenix (Lohse et al., 2008), Salt Lake City (Hall et al., 2014), southern Ontario (Zbieranowski and Aherne, 2012), and new work by the U.S. Geological Survey (USGS) in Denver generally indicate higher deposition of both oxidized and reduced forms of N in urban environments compared to surrounding rural areas.

Contrary to ambient air quality monitoring in urban areas, there is a paucity of wet deposition data for urban environments in the USA. Wet deposition monitoring by the NADP generally avoids urban areas in favor of collecting regionally representative data. Currently, only 7% (19 of the 261) NADP/NTN sites are classified as “urban”. The historical focus of the NADP/NTN on rural sites allowed for representative measurements from rural and isolated areas to be extrapolated across the entire U.S. landscape. However, this extrapolation fails to capture any urban-rural deposition gradients. NADP wet deposition maps therefore likely underestimate rates of deposition in urban areas (Howarth, 2007; Redling et al., 2013; Elliott et al., 2007; Rao et al., 2014), which has implications for determining impacts to water quality (Howarth, 2007).

The first step toward better understanding of urban wet and dry deposition across the U.S. is to increase the number of NADP/NTN sites in major metropolitan areas (Rao et al., 2014; Decina et al., 2017), which likely represents a long-term effort. This will require wet and dry deposition studies aimed at determining proper selection of monitoring locations with respect to urban emission sources, meteorology, and vegetation and other landscape characteristics. In the near-term, the use of ion exchange resin (IER; Fenn et al., 2018b) sampling of bulk N deposition and throughfall could be expanded in urban areas and along urban-to-rural transects to better define spatial and temporal variability of urban N deposition and guide site selection for new NTN monitoring.

Advances in atmospheric modeling are also needed to more accurately simulate deposition within urban areas and along urban-to-rural gradients. Improved representation of urban emissions, transport, and deposition in CTMs is a longer-term goal that will require targeted studies to understand emission and deposition processes as well as spatial variability of air concentrations. In the near term, the latter could be informed by supplementing existing urban monitoring of NO_2 with more spatially dense low-cost passive sampling (e.g., NO_2 , NH_3) to better characterize heterogeneity of N compounds within the urban atmosphere. Also, the TDep MMF method should be adapted to include monitoring data from existing urban monitoring sites listed in Appendix A.

3.1.1.5. Throughfall. Throughfall sampling is a widely used method to measure the net inputs of ions (e.g., NH_4^+ , NO_3^- , SO_4^{2-} , and base cations) from the atmosphere to the ground by collection of precipitation under a canopy of vegetation. Throughfall incorporates wet and some dry deposition as the ions that have accumulated on the vegetative surfaces are washed into the sampler by precipitation, reflecting the combined processes of deposition, as well as uptake, transformations, and leaching within the canopy (Draaijers et al., 1996; Bleeker et al., 2003; Fenn and Poth, 2004; Hansen et al., 2013a; Clarke et al., 2016; Fenn et al., 2018b). Throughfall is generally collected by a funnel that directs the sample into a collection container and is calculated in $\text{kg ha}^{-1} \text{ yr}^{-1}$ based on

the diameter of the funnel, ion concentration, and the volume of ionic solution. These samplers have also been used in open, canopy-free sites to collect bulk deposition (i.e. wet deposition and a portion of dry deposition). Due to ion loss through canopy flux, stemflow, and variations in canopy density, throughfall measurements provide a lower bound estimate of wet and dry deposition of inorganic N at a specific site. They provide a low-cost alternative to active deposition collectors that require electricity and weekly visits and can therefore be deployed in a more spatially dense manner.

In addition to characterizing deposition for ecosystem studies, additional studies employing throughfall and bulk measurements offer an opportunity to examine sub-grid processes and impacts of downscaling gridded deposition estimates from CTMs (Schwede and Lear, 2014; Williams et al., 2017) to specific locations. However, comparing site specific data to modeled output for a model grid (4–12 km) is challenging due to the ecological and geological diversity that exists within the model grid cell. To scale up from a single collector to a grid cell, or down from a model grid cell to a collector, it is necessary to further characterize throughfall methods to assess collector performance and in-canopy processes across canopy types and deposition regimes and to develop a method for relating throughfall to modeled deposition output. CTMs estimate deposition to the top of the canopy (i.e., canopy-scale inputs), whereas throughfall measurements reflect the net balance between deposition and in-canopy processes, complicating direct comparison. Thus, prior to detailed comparisons of throughfall to CTMs, studies are needed to better understand how throughfall measurements compare with canopy-scale direct measurements of dry + wet deposition.

Regarding further method development, a near-term goal is to develop a database of existing throughfall measurements for locations in the U.S., including both conventional and IER (Fenn et al., 2018b) methods. Such a database can be used to help better understand sampler performance and throughfall processes across a range of ecosystems with different vegetation types and density as well as relative contributions of wet versus dry deposition (e.g., see Fenn et al., 2013). In the longer term, additional analytical techniques are needed to measure dissolved ON by IER to capture the full inorganic/organic N budget. Concurrent measurements of throughfall N and bulk N deposition, and total canopy N flux measurements are needed in order to develop empirical relationships between throughfall and total N deposition. As a first step, these relationships could be examined by comparing throughfall to total deposition budgets comprising wet deposition plus site specific estimates of dry deposition derived from inferential models (Bytnerowicz et al., 2015). To understand the relationships between throughfall measurements and total deposition from gridded CTMs, a near-term objective is to use the throughfall database described above for measurement-model comparisons. Longer-term comparisons will require more comprehensive measurement datasets that capture model sub-grid variability and explicitly resolved wet and dry deposition versus in-canopy processes.

3.1.1.6. Satellite remote sensing of N compounds. The recent assessment of global precipitation chemistry and deposition by Vet et al. (2014) identified important monitoring gaps limiting the comparison of point surface measurements and gridded model estimates. These gaps included the limited spatial and temporal coverage of surface monitoring of air concentrations of important N species (e.g. NH_3 , HNO_3 , NO_2 , organic nitrates). Satellite remote sensing detection of atmospheric trace pollutants is a fast-evolving field that shows great promise for complementing existing surface monitoring data in this regard.

For N species, satellite products currently include NH_3 and NO_2 but do not account for other key species (particularly HNO_3 and organic nitrogen compounds) within the total N deposition budget. A number of recent studies have expanded on techniques coupling satellite observations with dry deposition schemes to estimate deposition or to provide

constraints for deposition estimates for NO₂ (Cheng et al., 2013; Lu et al., 2013; Nowlan et al., 2014; Kharol et al., 2018), total nitrate (in gaseous and particulate forms), NH₄⁺ (i.e., NH₄NO₃) (Jia et al., 2016), NOy (Geddes and Martin, 2017), and NH₃ (Kharol et al., 2018).

For applications to Nr deposition, current knowledge gaps in the remote sensing field fall into two categories: 1) improving and refining satellite-derived products to better represent surface air concentrations and 2) applying satellite derived lower tropospheric data products to estimate total Nr deposition budgets. The first represents a long-term research need, though there is currently a wide body of research focused on this problem. New instrument technologies and new missions will improve on spatial and temporal resolution and new data retrieval methods will help to optimize the data products. Additional research is needed to explore the use of remote sensing data to inform expanded surface monitoring for NH₃ and NO₂, to incorporate remote sensing data into MMF deposition methods, to improve the ability to use remotely sensed Nr species as surrogates for species that are not detectable from space, and to better understand the variability and uncertainty of emissions inventories for Nr compounds such as NH₃ (e.g., van Damme et al., 2018).

3.1.1.7. Monitoring network criteria for data sample validation and data completeness. Data validation protocols and completeness criteria are integral to ensure the quality of data from a monitoring network. In the case of the NADP/NTN, many of these protocols were developed near the beginning of the program based on best-management practices and therefore could benefit from scientific evaluation and possible revision. The NADP/NTN data validation protocols are used to screen records for potentially compromised data. Factors that can impact sample validation include operation of equipment and handling of samples in the field and in the laboratory (<http://nadp.slh.wisc.edu/data/ntn/meta/ntnDataValidation.pdf>). NADP/NTN completeness criteria are thresholds to limit the uncertainty in the calculated annual precipitation-weighted average (PWA) concentrations due to invalid data. Three completeness criteria are defined for the network as a whole and form the basis for the decision to include a site in the annual isopleth maps and seasonal data summary tables: (1) there must be valid concentrations for at least 75% of the summary period, (2) there must be precipitation amounts (including zero amounts) either from the rain gauge or from the sample volume for at least 90% of the summary period, and (3) there must be valid concentrations for at least 75% of the total precipitation amount reported for the summary period.

Once a site's record has been validated, the data are used to calculate annual PWA concentrations and deposition. A key aspect of calculating annual deposition is that weeks with missing concentrations use the annual PWA concentration determined from valid samples. On average the NADP/NTN wet deposition NH₄⁺ and NO₃⁻ concentrations exponentially decrease with increasing precipitation totals and are seasonally dependent, with lower concentrations in winter than summer. Substituting missing data with the annual PWA concentration does not account for these dependencies, which can increase the uncertainties and introduce systematic biases in the annual deposition values. Invalid samples generally occur more frequently at remote sites and locations that experience extreme weather conditions, such as high winds, blowing and drifting snow, and subfreezing temperatures, features typical of high alpine environments. When completeness criteria are not met, the annual deposition values for those sites are not included in the calculation of the NADP annual wet deposition raster data, which are used in the TDep mapping process.

An exploration of alternative completeness criteria, sample validation methods, and data substitution methods that would allow more sites and data to be included in annual deposition maps is warranted. Inclusion of more sites and improvement in the data substitution methods, especially for high-altitude and other challenging sites, may improve the spatial representativeness and accuracy of the TDep

maps. In the near term, research is needed to re-evaluate the definition of contaminated samples (i.e., samples that need to be excluded) and to identify samples with potential systematic biases that meet current criteria but should be invalidated. Research is also needed to improve the replacement of missing data, including data replacement with measurements from nearby sites and accounting for average seasonal and precipitation dependencies in sample concentrations. Improved statistical treatments and extrapolation methods for the mapping products are needed. Over the longer term, new sampling techniques and strategies (e.g., debris exclusion and using backup bulk snow collectors, wind shields, and optical precipitation sensors) may also be needed to augment current methods to make data records more complete.

3.1.2. Process measurements

3.1.2.1. Net air-surface exchange. Ammonia is an important component of the Nr deposition budget in many areas of the U.S. and differs from Nr compounds such as HNO₃ in that it is exchanged bi-directionally between the atmosphere and biosphere. The net exchange between the surface and the atmosphere is governed by the compensation point, the surface being a sink for atmospheric NH₃ when the atmospheric concentration exceeds the compensation point and a source of NH₃ under the opposite condition. As described in more detail in Section 3.2.4, compensation points are a function of temperature and the concentrations of NH₄⁺ and H⁺ in solution within (i.e., apoplast) and on the surface of leaves (i.e., cuticle) and in the soil pore water. Vegetation and soil exchange pathways are regulated by NH₃ emission potentials that vary by vegetation and soil type along with other aspects of ecosystem biogeochemistry (Massad et al., 2010; Zhang et al., 2010). Cuticular exchange processes are affected by surface wetness and the acidity of the exchange surface, which is influenced by the vegetation itself as well as the chemical composition of material deposited to the surface (Flechard et al., 1999; Burkhardt et al., 2009; Burkhardt and Hunsche, 2013; Wentworth et al., 2016). The reader is referred to Flechard et al. (2013) and references therein for a detailed review of the processes of NH₃ air surface exchange.

Bi-directional NH₃ air-surface exchange algorithms used in North American deposition assessments, both at the field scale (Li et al., 2016) and within gridded CTMs (Zhang et al., 2010; Bash et al., 2013; Zhu et al., 2015; Whaley et al., 2018), are largely based on parameterizations developed from European datasets (see Massad et al., 2010 and Flechard et al., 2013 and references therein). Because net ecosystem fluxes will vary with biogeochemistry, atmospheric composition and climatology, datasets are needed to assess seasonal and annual net fluxes of NH₃ and to validate or revise current parameterizations for North American conditions. Additional measurements are needed in forest ecosystems in general, including measurements that elucidate the role of decaying leaf litter as a component of the net canopy-scale flux (Hansen et al., 2013b, 2017). Studies are needed within and downwind of agricultural areas to better characterize net NH₃ fluxes in surrounding natural ecosystems experiencing elevated NH₃ concentrations. Measurements needed to support further improvement of model parameterizations for cuticular exchange and compensation points are further discussed in Sections 3.1.2.2 and 3.2.4, respectively.

Air-surface exchange of Nr and carbon are linked through biogenic emission processes and chemistry within the canopy air-space (Min et al., 2014). Evidence has accumulated that many gaseous biogenic species, not only NH₃, exhibit bi-directional exchange with vegetation (Kesselmeier, 2001; Rottenberger et al., 2004, 2005; Karl et al., 2005, 2010; Jardine et al., 2008, 2011; Park et al., 2013, 2014; Niinemets et al., 2014). Both upward and downward fluxes of fine particles above canopies are now routinely measured (Nemitz et al., 2004; Pryor et al., 2008a, 2013; Vong et al., 2010; Gordon et al., 2011; Lavi et al., 2013; Farmer et al., 2006, 2013; Deventer et al., 2015; Rannik et al., 2016). Observations of upward fluxes of gas phase oxidized nitrogen compounds, including NO₂ and peroxy-nitrates (Min et al., 2014;

Farmer and Cohen, 2008) illustrate the influence of in-canopy chemistry on net canopy-scale fluxes of Nr in forests. These studies challenge the fundamental conceptual framework of air-surface exchange employed in CTMs, that particulate matter and oxidized forms of gas phase Nr (other than NO) always deposit from the atmosphere to the surface. Additional studies such the Biosphere Effects on Aerosols and Photochemistry Experiment (BEARPEX, Farmer and Cohen, 2008; Wolfe et al., 2009; Min et al., 2012), designed to quantify within- and near-canopy sources and sinks of the components of the Nr chemical systems (e.g. NO_y and HNO₃-NH₃-NH₄NO₃), are needed across a range of North American ecosystems.

Given the complexity of the processes involved, long-term measurements will be required to fundamentally advance models to accurately simulate the magnitude and direction (e.g., emission or deposition) of net canopy-scale fluxes. Low cost methods such as COTAG (Section 3.1.1.2) are practical for characterizing spatial patterns of deposition for the primary Nr species at seasonal to annual timescales at a relatively large number of sites. However, establishment of a smaller number of long-term intensive sites (e.g., Harvard Forest, Munger et al., 1996; NitroEurope 'Level 3' sites, Skiba et al., 2009) in key ecosystems is needed to provide more detailed speciation of the deposition budget and to investigate the interactions between ecophysiology, atmospheric composition, and climate that drive annual and interannual fluxes.

3.1.2.2. Surface wetness and air-surface exchange. Surface wetness impacts the deposition of soluble compounds (van Hove et al., 1989) and therefore the rates and composition of Nr deposited to ecosystems. Compounds such as NH₃ may be reemitted as the surface dries. The surface wetness thus acts as a temporary reservoir that convolutes the origin of Nr, the quantifications of which are necessary to identify and mitigate Nr deposition issues. Wetness of vegetated surfaces can be classified as either "macroscopic" or "microscopic". The former includes dew, guttation, and precipitation, and the latter refers to the thin layer of moisture, invisible to the naked eye, that is maintained on the leaf surface by condensation of transpired water on the cuticle and previously deposited particles (Burkhardt and Hunsche, 2013). Precipitation is an intermittent macroscopic surface wetness while dew and guttation are diurnal processes occurring primarily at night. Dew formation is a meteorological phenomenon resulting in the condensation of atmospheric water vapor on leaf surfaces, whereas guttation is a plant physiological process involving the exudation of chemically diverse (Singh and Singh, 2013) plant water from the leaf surface. Microscopic wetness is hypothesized to permanently exist in some cases and is likely universal across vegetation types (Burkhardt and Hunsche, 2013).

While rain is an important intermittent source of surface wetness, processes of macroscopic wetness relevant to recurring diurnal cycles of air-surface exchange are driven by dew and guttation. Wentworth et al. (2016) recently demonstrated the role of dew as a temporary reservoir for NH₃ by measuring its volume and ion balance along with the dynamics of wetting and drying of the surface in relation to atmospheric NH₃ concentrations in a grass field. At their site, dew composition suggested that nearly all NH₄⁺ in the dew was emitted to the atmosphere as NH₃ during evaporation. An important implication of their work is that NH₃ deposited to the wet surface at night does not necessarily remain in the ecosystem.

In the short term, more studies similar to Wentworth et al. (2016) are needed for a range of vegetation characteristics, atmospheric acidity, and atmospheric NH₃ concentrations. Coupling of experiments investigating dew formation and chemistry with high temporal resolution measurements of NH₃ air concentrations and fluxes could provide valuable insight about the role of surface wetness in the net flux of NH₃ into and out of the ecosystem on time scales of days to weeks. In the long term, easily-implemented methods are needed to measure the volume of macroscopic surface wetness in more complex settings (i.e., forests) and to characterize its ionic composition. Studies which assess the

relative importance of dew versus guttation with respect to chemistry and wetness volume, and relationships between wetness dynamics and plant physiology are also needed (Hughes and Brimblecombe, 1994).

In addition to better understanding exchange with dew/guttation, a more complete understanding of the chemistry and dynamics of microscopic surface moisture, and its relation to the daytime leaf cuticular resistance (see Section 3.2.4), is also needed (Flechard et al., 2013; Burkhardt and Hunsche, 2013). Collecting temporal information on chemistry as macroscopic wetness becomes more concentrated during morning evaporation may help to inform the characteristics of cuticle surfaces in the absence of dew/guttation. Tools for directly examining the chemistry of microscopic moisture layers under field conditions are needed. As noted by Flechard et al. (2013) in a recent review of NH₃ bi-directional exchange models, laboratory experiments employing environmental microscopy (e.g. Burkhardt et al., 2012) may be informative in the absence of field measurements. In the near term, measurements of dew volume and chemistry will facilitate the testing of surface moisture predictions and more representative parameterization of cuticular resistance schemes used in gridded CTMs (e.g., Pleim et al., 2013; Zhang et al., 2010). Development of climatologies of surface wetness (Klemm et al., 2002) would be helpful in this regard. While the discussion here focuses on NH₃, better understanding of the impact of surface wetness on exchange processes is needed for other Nr compounds as well (e.g., PANs, Turnipseed et al., 2006).

3.1.2.3. Speciation of atmospheric organic nitrogen. ON is a general term for a large class of compounds containing both nitrogen and carbon that are present in the gas phase, aerosol and precipitation and include both primary emitted compounds and secondary reaction products (Neff et al., 2002; Cape et al., 2011; Cornell, 2011; Jickells et al., 2013). While routine measurements of bulk ON in precipitation and PM are needed to improve deposition budgets, more complete speciation of ON is needed to characterize its sources and processes of air-surface exchange. Though the sources of ON emissions are not fully understood, soils/dust, biomass burning, marine, agricultural, and various anthropogenic sources have been identified as important (Jickells et al., 2013 and references therein). The need to better understand ON compounds from an ecological perspective is motivated by their significant contribution to Nr deposition, previously noted. While new measurement techniques are rapidly increasing understanding of atmospheric ON, several important knowledge and data gaps persist, including: incomplete speciation and quantification across the gas, aerosol and precipitation phases; limited spatial and temporal range of speciated measurements; and lack of standardized sampling and measurement protocols for speciating ON.

Mass spectrometry (MS) is one of the most common methods for speciation of ON in the gas and aerosol phases. Gas chromatography (GC) and proton-transfer-reaction (PTR)-MS are commonly used for real-time measurements. Classes of gas phase ON species commonly detected by GC-MS include alkyl nitrates and peroxyacyl nitrates (Koppmann, 2007). Acetonitrile (CH₃CN) and hydrogen cyanide (HCN) are two gas phase species commonly measured by PTR-MS (de Gouw et al., 2003; Schneider et al., 1997). HCN is also measured by other GC methods (Ambrose et al., 2012; Singh et al., 2003). Chemical ionization mass spectrometry (CIMS) has been used to measure inorganic nitrogen containing compounds (HNO₃, HO₂NO₂, NH₃) and organic species such as PAN, peroxypropionyl nitrate (PPN), peroxyethacryloyl nitrate (MPAN), HCN, and amines (Huey, 2007) as well as isocyanic acid (Roberts et al., 2010). CIMS has been applied to directly measure air-surface exchange of gas phase ON species, including PAN, PPN, and MPAN (Wolfe et al., 2009, 2015; Turnipseed et al., 2006; Min et al., 2012), isoprene nitrates (Nguyen et al., 2015), isoprene and monoterpene nitrooxy hydroperoxides (Nguyen et al., 2015), hydroxy nitrates of methacrolein and methylvinylketone (Nguyen et al., 2015), and HCN (Nguyen et al., 2015) at a few sites in the U.S. Mass spectrometry has also become a popular tool for online

characterization of organic compounds in aerosols, including ON, though fragmentation limits speciation (Lee et al., 2016a; Schurman et al., 2015a, 2015b; Zhang et al., 2015; Farmer et al., 2010). Air-surface exchange of peroxy-nitrates and total gas + particulate alkyl nitrates have also been measured by thermal desorption, laser induced fluorescence (TD-LIF, Farmer et al., 2006; Min et al., 2012) at Blodgett Forest in California.

Some of these gas phase real-time techniques can also be used for offline detection of ON species in aerosols and precipitation (Mandalakis et al., 2011; Timkovsky et al., 2015). Organo-nitrate compounds are commonly detected by analysis of solvent extracted filters either by GC (O'Brien et al., 1995) or FTIR (Nielsen et al., 1998). Liquid chromatography (LC-MS) techniques have been applied for amino acids (Matos et al., 2016; Samy et al., 2011), urea, and amines (Samy and Hays, 2013; Place et al., 2017), and nitrocatechols and nitrophenols (Desyaterik et al., 2013), and can be coupled with electrospray ionization (ESI) MS for determination of ion fragments indicative of ON compounds (Zhang et al., 2015). Altieri et al. (2016) used ultra-high resolution electrospray ionization Fourier transform-ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) to identify 750 ON compounds. 2-dimensional gas chromatography with time of flight mass spectrometry (GCxGC-TOF-MS) and nitrogen chemiluminescence detection (Özel et al., 2010, 2011) is a relatively comprehensive method for speciation of ON in aerosols.

While significant progress has been made in the development and application of techniques to speciate atmospheric ON, development of a complete understanding of the contribution of individual species to total ON in Nr deposition remains challenging due in part to some of the limitations listed below. Progress in this endeavor will require closer collaboration between research groups specializing in measurements of different compounds and classes of compounds to simultaneously speciate a larger fraction of the ON budget than is typically possible by individual investigators. Greater collaboration between the measurement and modeling communities would also help to design studies that target the most important ON sources, atmospheric processes, and receptor ecosystems.

An important limitation is the lack of method evaluation and inter-comparison for ON speciation (Timkovsky et al., 2015). For example, collocated measurements of bulk particulate organic nitrates can differ substantially (Lee et al., 2016a). The determination of which methods are best suited for ON speciation (gas, aerosol, precipitation; offline versus real-time) is a high priority that could be met in the near-term by compiling information on which techniques have been used and considering their pros and cons. This is an important first step toward standardization of procedures and protocols for the most widely used methods, which is a longer-term goal. As part of this process, field studies to investigate tradeoffs in data coverage between real-time versus offline approaches and assess uncertainties would be useful. This would be an opportunity to measure a complete ON budget (gas, aerosol, and precipitation) at a specific site with collaborators who specialize in bulk ON measurements and specific classes of compounds in gas, aerosol, and precipitation. Finally, additional method development may be needed to apply online systems for new speciation to measurements of air-surface exchange.

3.1.2.4. Deposition to snow. Snow serves as a reservoir of water and Nr for many ecosystems during the winter season and influences soil moisture and temperature, decomposition, Nr mineralization, plant function, and length of the growing season by the timing of snowmelt (Bowman, 1992 and references therein). Alpine environments are located at high-altitude where snow covers the landscape for large portions of the year (Kuhn, 2001). Wet deposition in the form of snow and dry deposition to the snow surface must both be characterized for accurate total Nr deposition estimates in these sensitive high-altitude ecosystems, where critical loads for environmental effects are typically low (1 to 5 kg N ha⁻¹; Pardo et al., 2011; Nanus et al., 2012). The complex terrain typical of alpine

environments can induce highly spatially variable patterns of precipitation and meteorology and, subsequently, deposition. Furthermore, the remoteness and difficult terrain characteristic of alpine ecosystems makes sampling and establishment of monitoring sites logistically challenging and costly. Improvements to existing measurement and data validation methods as well as new spatially intensive measurements are needed to understand the representativeness and accuracy of historical NADP measurements at high-elevation sites (see Section 3.1.1.7). Additionally, detailed measurements are needed to better understand the importance of dry deposition, surface chemistry, and snowmelt processes to improve models of deposition to snow covered surfaces.

In the near term, improvements in monitoring technology and techniques to obtain more representative measurements of wet deposition as snow would include a reassessment of NADP data validation and completeness criteria for high elevation sites; use of weekly bulk snow samples collocated with NADP sites to be used in cases when NADP samples are missed due to equipment failure; use of wind-shielded wet deposition collectors to limit wind-blown secondary snow deposition (Wetherbee and Rhodes, 2013); and use of independent precipitation gages not impacted by wind-redistributed snow to correct snow-deposition measurements (Williams et al., 1998).

Deployment of bulk measurement methods to characterize spatial variability and deposition processes could also be accomplished in the near term using existing technology. Approaches could include the use of IER throughfall/bulk deposition collectors to augment summer deposition measurements (Clow et al., 2015); measurement of snowpack chemistry to augment winter total deposition measurements (Clow et al., 2002); use of passive sampler methods to characterize spatial variability of air concentrations to inform dry deposition estimates; measurement of bulk snow surface minus NTN weekly concentration differences to estimate dry deposition; and the use of lysimeters to characterize the Nr content, transformations, and subsurface movement of the snowpack during melting.

New measurements are needed to better understand the importance of dry deposition, surface chemistry, and snowmelt processes and to improve models of deposition to snow covered surfaces. A near-term goal would be to prioritize deposition model uncertainties (e.g., wet scavenging, gas exchange, and particulate deposition) to guide needed measurements. Given the difficulty and expense of process-level flux experiments, the measurements themselves would represent a longer-term goal focused broadly on direct flux measurements to quantify dry deposition and re-emission coupled with snow measurements to assess the roles of surface wetness and chemistry. Furthermore, while the discussion here focuses on alpine ecosystems, better understanding of deposition to snow is important in other environment as well, such as urban locations with known air quality issues (e.g. Salt Lake City, UT; Fairbanks, AK) during winter.

3.1.2.5. Occult deposition. Deposition of pollutants by cloud water (i.e., occult deposition) exceeds deposition by precipitation and dry deposition in high elevation settings from North Carolina to Maine (Isil et al., 2000). In high elevation environments, cloud water samples are typically 5 to 20 times more acidic than rain water (Mohnen and Vong, 1993; Mohnen et al., 1990; Vong et al., 1991) and the interception of cloud water by spruce and fir trees and other vegetation in the Appalachian Mountains has been shown to be a major deposition pathway (Aneja and Kim, 1993; Miller et al., 1993; Lindberg, 1992; Lovett and Kinsman, 1990). The large loading of pollutants in such environments is due to a combination of factors such as high frequency of cloud immersion, high wind speeds, orographic enhancement of precipitation, and large leaf areas of tree species typical of these environments (Miller and Friedland, 1999). Deposition of Nr in fog or cloud water is also a very important N input pathway in forests along the coast of California (redwood forests), the Transverse ranges of southern California (i.e., inland from LA), and in the western Sierra Nevada (Collett et al., 1990; Fenn et al., 2000; Templer et al., 2015).

Development of accurate Nr deposition budgets for ecosystems impacted by occult deposition requires reliable measurements of cloud and fog water. However, the cost and labor intensity of cloud water sample collection has made long-term deposition studies at single and multiple sites or on a network-wide basis extremely difficult. Two small cloud water monitoring networks existed in the late 1980s and the mid-1990s through 2011 in the eastern U.S. (Mohnen et al., 1990; Isil et al., 2017). Both of these efforts were discontinued due to the cost of operating at remote locations (mountain tops). These obstacles have limited the routine collection of cloud water samples on a broader geographic scale, and most existing data have been collected during the growing season at eastern U.S. locations (Isil et al., 2017). National monitoring infrastructure remains insufficient to conduct long-term mountain-top measurements.

Establishing a network of sites dedicated to permanent sampling in coastal or other fog prone areas in the eastern and western U.S., as well as a few interior high-elevation sites, is needed but represents a long-term goal. A significant hurdle is the development of a cost-effective cloud deposition sampler that is deployable in a routine monitoring network. In the shorter term, use of existing data to develop empirical models of cloud deposition as a fraction of total deposition may be helpful. From a process standpoint, there remains a need to investigate the role of cloud drop size in occult deposition, which can impact the chemical composition of cloud water as well as deposition rates. Finally, representation of occult deposition in CTMs is an important long-term goal.

3.2. Modeled Nr deposition budgets

Measurements of nitrogen deposition are typically incomplete with respect to speciation of the Nr pool, are often limited in spatial representativeness, and may lack temporal coverage sufficient to develop representative annual budgets. Models are therefore needed to develop annual deposition estimates across the range of spatial (Fig. 5) and temporal scales (seasonal to annual) relevant to critical loads assessments. Spatial scale is an important consideration in assessing uncertainty in deposition estimates (Fig. 5) and the methods used to develop budgets for each spatial scale have uncertainties that propagate from

measurements to models, across scales (from field to model grid to region), and over time.

3.2.1. Chemical transport models

Chemical transport models commonly used for North American Nr deposition assessments include the Community Multiscale Air Quality model (CMAQ, Byun and Schere, 2006; Zhang et al., 2018a, www.epa.gov/cmaq), Global Environmental Multiscale model – Modeling Air quality and Chemistry (GEM-MACH; Moran et al., 2017; Makar et al., 2018), Comprehensive Air Quality Model with Extensions (CAMx, Thompson et al., 2015; Zhang et al., 2018b), and the Goddard Earth Observing System – Chemistry model (GEOS-Chem, Lee et al., 2016b). CTMs require inputs for meteorological variables, land use and vegetation characterization, and emissions and must properly simulate atmospheric chemistry and physics to accurately predict Nr deposition (Fig. 5). To the extent possible, CTMs try to represent processes using first principles, but limitations in understanding of processes and restrictions on computational efficiency sometimes require that empirical parameterizations and approximations are used instead. As described in Section 2.0, the U.S. has experienced a large-scale shift in atmospheric chemistry over the last two decades: reduced and organic forms of nitrogen are becoming increasingly important components of total deposition budgets as NO_x emissions have dramatically declined (Li et al., 2016). This has implications for CTMs with respect to modernizing and improving emission inventories, chemical mechanisms, and deposition algorithms relevant to Nr.

3.2.2. Emissions

Emissions are fundamental inputs to CTMs and their uncertainties propagate through the modeling system. With respect to Nr deposition budgets, improvements to NH₃ emission inventories for agricultural sources are urgently needed to improve the representation of ambient NH₃ concentrations and deposition in CTMs (Heald et al., 2012; Nowak et al., 2012; Walker et al., 2012b; Paulot et al., 2014; Battye et al., 2016; Bray et al., 2017). In the U.S., NH₃ emissions from CAFOs are estimated by applying animal and management specific emission factors to county-level animal population data to produce daily county-level emissions (National Emissions Inventory, U.S. EPA,

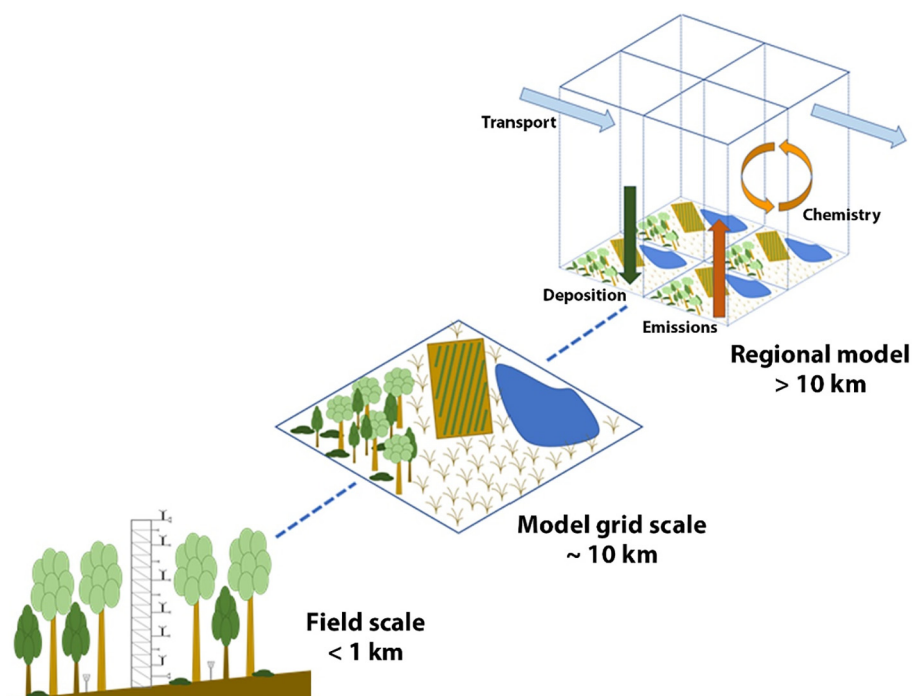


Fig. 5. Spatial scales of deposition budgets used in critical loads assessments. Adapted from Walker et al. (2019b).

2014; McQuilling and Adams, 2015; Pinder et al., 2004). The NH_3 emissions are then processed through the Sparse Matrix Operator Kernel Emissions (SMOKE) model (<https://www.cmascenter.org/smoke/>) to provide gridded hourly emissions for use in CTMs such as CMAQ. For fertilized soils, the Fertilizer Emission Scenario Tool for CMAQ (FEST-C, <https://www.cmascenter.org/fest-c/>) simulates daily fertilizer application using the Environmental Policy Integrated Climate (EPIC) model (Cooter et al., 2012). Soil biogeochemistry simulated in EPIC provides temporally and spatially resolved estimates of the soil NH_3 emission potential, which is used within the CMAQ bi-directional modeling framework (Bash et al., 2013) to provide hourly NH_3 emissions from fertilized soils.

For CAFOs, improvements are needed in estimates of the emissions themselves as well as their spatial and temporal allocation at the sub county-scale (e.g. facilities in Sampson county shown in Fig. 4), which will ultimately require information on emissions at the facility scale. This is a long-term goal that will require close collaboration with industry stakeholders, U.S. Department of Agriculture (USDA) and other federal agencies, as well as academic institutions. For emissions from fertilized soils, additional studies are needed to evaluate EPIC NH_3 emission potentials against soil biogeochemical N measurements and NH_3 fluxes for a wider range of soil and fertilizer types (Cooter et al., 2010) including increased N efficiency formulas, application methods, and soil types. Close collaboration between the measurement and modeling communities is needed to ensure that field studies directly address the highest priority modeling needs.

Improvement of inventories of mobile NO_x emissions is also needed, particularly to address potential overestimates during summer (McDonald et al., 2012; Anderson et al., 2014; McDonald et al., 2018). Inventories for mobile NH_3 emissions are also in urgent need of refinement, as recent measurements suggest emissions may be underestimated by a factor of 2 in the U.S. (Sun et al., 2017). Better characterization of emissions of dust-derived nonvolatile cations, which impact the gas/aerosol partitioning of inorganic NO_3^- and NH_4^+ , is needed to improve aerosol thermodynamic models (Appel et al., 2013; Pye et al., 2018; Vasilakos et al., 2018; Guo et al., 2018). For reduced forms of organic nitrogen, better understanding of emissions of amines (Murphy et al., 2007; Ge et al., 2011; Kuhn et al., 2011; Yu et al., 2012; Almeida et al., 2013; Sintermann et al., 2014) represents an important long-term effort.

3.2.3. Atmospheric chemistry

Simulation of Nr deposition requires accurate representation of the multitude of inorganic and organic Nr species in the atmosphere. This includes speciation between the gas and aerosol phases, which, owing to the larger deposition velocity of gases, directly affects dry deposition rates. The Nr system can be broadly categorized into oxidized (NO_y) and reduced (NH_3 , NH_4^+ , amines) components. One of the most uncertain aspects of gas-phase NO_y chemistry is the fate of organic nitrates, which includes photolysis, oxidation, partitioning to the particulate phase, hydrolysis, and deposition. These processes have dramatic differences in terms of their implications for O_3 and PM formation and deposition as photolysis decomposes some ON back to NO_x and hydrolysis results in HNO_3 . Historically (e.g. CMAQ v5.0.2, released in 2014, and prior), hydrolysis of organic nitrates on or in particles was not considered by models, but recent work indicates organic nitrates contribute significantly to secondary organic aerosol (SOA) formation (Pye et al., 2015; Xu et al., 2015; Lee et al., 2016a; Ng et al., 2017), have short particle-phase lifetimes (Lee et al., 2016a) and could be largely lost to HNO_3 via heterogeneous hydrolysis (Fisher et al., 2016). Standard chemical mechanisms used in CTMs do not explicitly include hydrolysis of organic nitrates, however this is being added to some specialized versions as understanding improves. The chemistry of N_2O_5 is another key model uncertainty. In winter, N_2O_5 hydrolysis to HNO_3 controls the lifetime of NO_x (Kenagy et al., 2018). However, current CTM parameterizations generally fail to capture the range of atmospherically relevant

N_2O_5 reaction probabilities and often overpredict the conversion of N_2O_5 to HNO_3 (McDuffie et al., 2018), one of the fastest depositing Nr species.

Amines represent an uncertain aspect of NH_x chemistry. These ON compounds are generally not represented in models but are recognized contributors to the organic component of $\text{PM}_{2.5}$ and particle nucleation. Amines can react in the atmosphere with HNO_3 and H_2SO_4 to form salts (Murphy et al., 2007). Recent research is also focusing on understanding the role of amines in new particle formation (Yu et al., 2012; Almeida et al., 2013) and in the formation of SOA (Murphy et al., 2007; Price et al., 2014) and developing chemical mechanisms to describe the atmospheric chemistry so that their importance to deposition may be better understood.

3.2.4. Dry deposition algorithms

Field-scale soil-vegetation-atmosphere transfer models (referred to herein as 'field-scale' models) are used to develop site-specific dry deposition budgets, examine air-surface exchange processes, and generalize dry deposition parameterizations to forms suitable for incorporation into CTMs.

Parameterizations of air-surface exchange processes used in current CTMs were initially developed in the 1970's-80's based on wind tunnel and field measurements (Hicks et al., 2016). These simple parameterizations, which separate emissions and deposition processes, have not substantially changed in the intervening decades. Many of the approaches used in CTMs and field-scale inferential models employ the resistance paradigm (Wesely, 1989), which treats each pathway between the atmosphere and surface as a set of resistances that act in series or parallel. The dry deposition velocity, V_d , is calculated as

$$V_d = \frac{1}{R_a + R_b + R_s} \quad (1)$$

where R_a is the aerodynamic resistance, R_b is the quasi-laminar boundary layer resistance, and R_s is the surface resistance. Taking the generalized uni-directional dry deposition scheme for gases shown in Fig. 6a as an example, R_s can be further subdivided into its components, including the stomatal (R_{st}), mesophyll (R_{mes}), cuticular (R_w), in-canopy aerodynamic (R_{ac}), and ground (R_g) resistances. Resistance models for particle deposition incorporate terms for gravitation settling and other processes including Brownian diffusion, interception and impaction (Khan and Perlinger, 2017).

Comparisons of inferential models (Flechard et al., 2011; Schwede et al., 2011; Li et al., 2016) and algorithms used in CTMs (Saylor et al., 2019; Khan and Perlinger, 2017; Giardina and Buffa, 2018; Wu et al., 2011, 2012) illustrate the high degree of complexity in dry deposition parameterizations and a lack of understanding of many of the important dry deposition processes. Deposition velocities and fluxes for Nr dry deposition may differ by a factor of 3 or more (Flechard et al., 2011; Li et al., 2016) among field-scale models. While the processes that control the atmospheric (R_a , R_b) and stomatal (R_{st}) resistances are fairly well understood for gas phase compounds, there is much less fundamental understanding of the exchange processes that occur at the leaf cuticle (R_w) and the ground (R_g) (i.e., non-stomatal pathways). The role of surface wetness as an important driver of non-stomatal exchange has been previously mentioned in the context of NH_3 fluxes, though better understanding of exchange with wet surfaces is needed for other Nr compounds as well (e.g., PAN, Turnipseed et al., 2006). These non-stomatal resistances (i.e., R_w , R_g) are typically parameterized from the residual R_s after R_a , R_b , R_{st} , and R_{mes} have been accounted for (Fig. 6a). The dynamics of R_w are often inferred from night time measurements when fluxes become more uncertain due to limited turbulent mixing. Without coincident flux measurements above and below the canopy, behavior of R_g is difficult to infer from net canopy-scale fluxes, particularly in deep canopies, due to vertical gradients in R_{ac} and the confounding effects of other non-stomatal processes. Thus, parameterizations

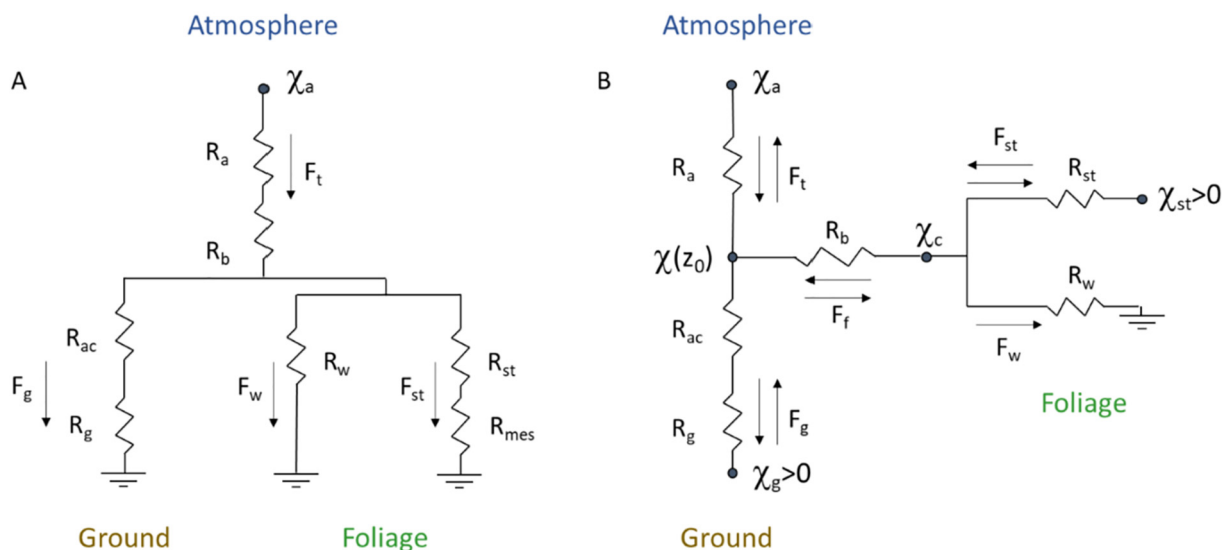


Fig. 6. Resistance diagrams for generalized unidirectional dry deposition model for gases (A) and bi-directional modeling framework for NH_3 (B, adapted from Nemitz et al., 2001). Fluxes (F), resistances (R), and concentrations (χ) are shown.

remain highly uncertain due to a lack of understanding of the underlying processes. There is a critical need for field studies designed to improve model parameterizations of non-stomatal processes.

The bi-directional exchange of NH_3 is increasingly being included in CTMs (Zhang et al., 2010; Wichink Kruit et al., 2012; Pleim et al., 2013; Bash et al., 2013; Zhu et al., 2015), but the underlying parameterizations remain uncertain. Since NH_3 can be emitted or deposited depending on the compensation point of the underlying surface, failure to consider the bi-directionality can cause biases in modeled fluxes. A commonly used framework for bi-directional modeling is the two-layer resistance model of Nemitz et al. (2001, Fig. 6b), in which the competing processes of emission and deposition fluxes (F) within the foliage (vegetation, F_f) and ground (F_g) components are taken into account by relating the net canopy-scale NH_3 flux (F_t) to the surface concentration ($\chi(z_0)$). For this framework, the stomatal (χ_{st}) and ground (χ_g) compensation points (Fig. 6b) are determined as a function of temperature (T) and the aqueous concentrations of NH_4^+ and H^+ in the leaf apoplast or soil pore solution ($[NH_4^+]$, $[H^+]$) using, for example, the approach of Nemitz et al. (2001):

$$X_{st,g} = \frac{161500}{T} \exp\left(-\frac{10378}{T}\right) \frac{[NH_4^+]}{[H^+]} \quad (2)$$

The stomatal and soil emission potentials ($\Gamma_{st,g}$) are represented by the ratio of $[NH_4^+]$ to $[H^+]$ in solution. Higher $[NH_4^+]$ and lower $[H^+]$ (i.e. higher pH) would correspond to higher $\Gamma_{st,g}$ and $\chi_{st,g}$. The reader is referred to Massad et al., 2010 and references therein for a review of commonly used parameterizations for the bi-directional NH_3 flux framework.

Γ_{st} and X_{st} may be estimated from canopy-scale flux measurements (Flechard, 1998) and enclosure-based gas exchange measurements (Hill et al., 2001) or measured by extraction and analysis of the leaf apoplast solution (Husted et al., 2000). Given the difficulties of extracting the apoplast directly, recent efforts have drawn on the relationships between the NH_4^+ content of the apoplast and leaf tissue to estimate X_{st} from bulk chemical analysis of vegetation tissue (Mattsson et al., 2009; Massad et al., 2010). Datasets of Γ_{st} , X_{st} and relevant leaf chemistry compiled by Zhang et al. (2010) and Massad et al. (2010) collectively illustrate that more information exists for managed (i.e., crops) versus unmanaged (i.e. natural/semi-natural) ecosystems. For natural ecosystems, grassland and other short vegetation (e.g., heathland) have been studied much more extensively than forests. Additionally,

existing data were primarily collected in European ecosystems. In North America, more data are needed to characterize X_{st} for natural systems, specifically forests. Measurements are needed over time during the growing season (i.e., leaf out, peak leaf area, senescence) and in ecosystems receiving a range of deposition, so that X_{st} parameterizations implemented in CTMs may incorporate temporal and spatial dynamics. Studies examining the relationship between bulk tissue and apoplast NH_4^+ (Massad et al., 2010) are needed to refine parameterizations for North American vegetation species.

Γ_g and X_g may be derived from measurements of the pH and NH_4^+ content of soil pore water (Nemitz et al., 2001). Comparisons of compensation points estimated from measured soil chemistry to measurements of air-surface exchange and gaseous NH_3 concentrations in the soil profile indicate that determinations of total soil extractable NH_4^+ using standard methods (i.e., 1 or 2 M KCl) may overestimate soil emission potentials (Nefel et al., 1998; Nemitz et al., 2001; Cooter et al., 2010). Alternatives for deriving more realistic estimates of Γ_g , including soil extraction with lower ionic strength solutions (Cooter et al., 2010) and modeling the adsorption characteristics of NH_4^+ in the soil matrix (Vogeler et al., 2010) warrant further exploration.

Γ_g is usually assumed to represent the soil. However, emission or uptake by decaying leaf litter on the soil surface is another potentially important process in natural ecosystems (Hansen et al., 2013b, 2017). Studies have shown that the emission potential of litter may be higher than the stomata and soil depending on the type of litter and extent of decomposition (David et al., 2009; Herrmann et al., 2009; Mattsson et al., 2009; Sutton et al., 2009). Measurements of litter chemistry are needed in a range of different natural ecosystems to better understand the potential importance of this emission process with respect to net ecosystem NH_3 fluxes and to inform necessary refinements to bi-directional exchange models (Hansen et al., 2017).

Regarding exchange of NH_3 with wet surfaces (see Section 3.1.2.2), the results of Wentworth et al. (2016) reinforce the need for continued evolution of the bi-directional NH_3 modeling framework to include cuticular emission (Sutton et al., 1998). Ignoring computational intensity, the primary challenge to further advancement of the dynamic wetness chemistry models of Flechard et al. (1999) and Burkhardt et al. (2009) is a lack of observational data needed to initialize and test the models. Current efforts rely on measurements of the bulk chemistry of relatively large droplets (i.e., macroscopic wetness, Section 3.1.2.2) collected at night and early morning or after rain events. Studies of dew chemistry and reemission of volatile compounds that consider the modeling framework of Burkhardt et al. (2009) and include chemical analyses

that will allow for extension of the results to this cuticular modeling framework would be particularly beneficial. Simplified versions will be needed, however, for eventual incorporation into CTMs.

Dry deposition of particles can be an important component of total N deposition, especially during periods or in locations with limited wet deposition. Most particle deposition velocity algorithms used in current CTMs have their heritage in the seminal work of *Slinn (1982)*, but algorithms derived from it can produce widely differing deposition velocities under identical conditions (*Khan and Perlinger, 2017; Flechard et al., 2011*) and can deviate substantially from measured fluxes (*Pryor et al., 2008b; Hicks et al., 2016*). Explanations for model-measurement discrepancies have been proposed (*Pryor et al., 2008b*), ranging from observational errors, to chemical flux divergences, faulty model assumptions, or the neglect of important deposition processes (e.g., turbophoresis, thermophoresis, etc.). Additional measurements are needed to resolve these differences and to reconcile differences in model algorithms, particularly for accumulation mode (0.1–2.0 μm diameter) particles above canopies with high surface roughness (i.e., forests).

While resistance-based schemes represent the state of the science for field-scale inferential dry deposition models and CTMs, recent studies call for advancement toward more complex modeling frameworks to incorporate in-canopy processes that result in upward fluxes (see *Section 3.1.2.1*) of particles and gas phase oxidized nitrogen (e.g., *Ganzeveld et al., 2002a, 2002b*). As air-surface exchange models incorporate more complex processes, model evaluation becomes increasingly important. Measurements of opportunity (e.g., the Southern Oxidant and Aerosol Study; *Xu et al., 2015*) are valuable for model evaluations but comprehensive (e.g., in-and above-canopy chemistry, fluxes, turbulence, biogeochemistry, surface characteristics) field measurement campaigns dedicated to improving these models will also be necessary. An important component of model evaluation will include intermodel comparisons such as the Canopy Exchange Model Intercomparison Project (CANEXMIP, <https://ileaps.org/current-projects>). Computational science research will be needed to develop techniques to condense comprehensive surface-atmosphere exchange models down to computationally viable modules appropriate for CTMs. Although the effort and resources required to implement an enhanced representation of surface-atmosphere exchange in CTMs is large, the benefit is significant and potentially critical to properly accounting for linkages between deposition, air quality, weather and climate in predictions of long-term ecosystem change.

3.2.5. Measurement-model fusion

In MMF, the predictions from a CTM are combined with network measurements to reduce biases in wet and dry deposition. In the U.S., the TDep MMF approach (*Schwede and Lear, 2014*) described in *Section 2* was developed as part of the activities of the NADP Total Deposition Science Subcommittee.

A slightly different approach has been developed by Environment and Climate Change Canada (ECCC). The ECCC project ADAGIO (Atmospheric Deposition Analysis Generated by optimal Interpolation from Observations/Analyse du Dépôt Atmosphérique Généré par Interpolation optimale des Observations) generates maps of optimized wet, dry and total annual deposition in Canada and the U.S., also by combining observed and modeled data. For nitrogen, measured concentrations of gas-phase HNO_3 , NO_2 , NO , and NH_3 ; particulate NO_3^- and NH_4^+ ; and NO_3^- and NH_4^+ in precipitation from Canadian and U.S. networks are used to adjust predicted concentrations from GEM-MACH using optimal interpolation, a statistical method for minimizing the differences between the model and measurements. This process generates maps of air and precipitation concentrations at a 10-km resolution. Dry deposition velocities derived from GEM-MACH are then applied to the adjusted concentration grids of gas and particle species to generate deposition fluxes of measured species. Wet deposition fluxes are calculated using precipitation amounts from the Canadian Precipitation

Analysis (CaPA) used at ECCC. CaPA uses the GEM weather forecast and adjusts daily precipitation amounts using climate station and radar observations, also using optimal interpolation methods. Dry and wet deposition fluxes of unmeasured species, such as N_2O_5 , HONO , PAN and organic nitrates, are taken from the model directly.

In the coming years, MMF techniques will benefit from the improvements in both measurements and models described in the previous sections. The use of satellite data in MMF approaches may provide more insight. This could include the use of satellite data for evaluation of model concentration fields, particularly for species such as NO_2 and NH_3 which are highly spatially variable, or to refine the spatial weighting of measurement versus modeled concentrations in the fusion process. Also, the spatial variability of NH_3 air concentrations and the bi-directional nature of NH_3 air surface exchange makes bias correction of concentration fields for MMF applications more difficult compared to other species (e.g., *Schwede et al., 2014*). Methods for bias correcting NH_3 concentrations or fluxes derived from CTMs are needed. Finally, land use specific deposition velocities and fluxes are more useful to the critical loads community than grid-averaged values. Adoption of techniques to quantify land use specific total deposition within MMF methods is needed.

3.3. Source apportionment of Nr deposition

3.3.1. Isotopic characterization of Nr

Methodological advances have facilitated the unprecedented examination of the isotopic composition of Nr species in the atmosphere, including NH_3 , NO_x , and NO_3^- (i.e., gaseous HNO_3 and aqueous HNO_3 and NO_3^-). This isotopic information can provide new insight into mechanisms of transformation and cycling of Nr in the atmosphere and help resolve the contribution of NO_x and NH_3 emission sources to deposition (see *Elliott et al., 2019*). While much progress has occurred during the past decade, further research is required to more fully apply isotopes to understanding atmospheric N chemistry and deposition. Existing studies demonstrate that isotopic ratios of atmospheric N have great promise to aid in source apportionment. However, the field needs further refinement before incorporation into regulatory frameworks.

Much of the needed future research will involve characterizing N isotopic signatures from emission sources. First, a more robust inventory of emission source signatures for NO_x and NH_3 emission sources is required. While a handful of studies now exist that document ranges in isotope ratios for major emission sources, source signatures have not been explored extensively for all sources. Variations and uncertainties in source signatures remain an issue in limiting their effectiveness in source apportionment studies, and observations that focus on mechanisms driving these variations (e.g., effects of catalytic reduction technologies on vehicular $\delta^{15}\text{N}$ - NO_x and $\delta^{15}\text{N}$ - NH_3 , $\delta^{15}\text{N}$ of soil-emitted NO and NH_3 as a function of soil and environmental conditions) are extremely limited. This research need is a high priority that could be pursued in the short-term.

Secondly, further research is needed to characterize atmospheric effects (i.e., fractionations) that can alter the fidelity of isotopic source signatures and the composition of ambient and/or deposited NO_y and NH_x . In addition to these efforts, more research, including additional gradient studies, are needed to address the effects of field conditions, geographic scale, atmospheric processes, and sampling protocols on resulting isotopic compositions of wet- and dry-deposited forms of NO_y and NH_x .

As understanding of the isotopic chemistry of atmospheric N evolves, isotopic ratios can also be useful for improvement and application of CTMs. For example, isotopic methods could be used to empirically validate the relative contributions of hard-to-quantify emission sources (e.g., lightning, soil NO emissions) and used as tracers to provide empirical validation of chemical reactions.

Finally, while $\Delta^{17}\text{O}$ - NO_3^- is a robust tracer of photochemical NO_3^- production in the atmosphere, there is also tremendous potential for

the application of $\Delta^{17}\text{O}-\text{NO}_3^-$ to understand the impact of atmospheric NO_3^- deposition on ecosystems, including streams and rivers. Given that $\Delta^{17}\text{O}$ is a conservative tracer, it can be used to quantify atmospheric NO_3^- contributions to water bodies, as well as quantify the effects of mass-dependent processes like denitrification. Expansion of this approach to quantify the relative proportion of atmospheric NO_3^- in streams and rivers beyond existing studies would help refine our general understanding of reactive N dynamics in watersheds and ecosystems (e.g. Rose et al., 2015; Michalski, 2003).

3.3.2. Source apportionment modeling

Source apportionment modeling plays an important role in the development of management strategies to reduce emissions and deposition of Nr. For example, attributing sources of nitrogen that contribute to deposition has been a key focus in attempting to quantify and manage excessive nitrogen loads to RMNP (Rodriguez et al., 2011; Gebhart et al., 2011; Thompson et al., 2015). CAFOs in northeastern Colorado have been shown to contribute to Nr deposition episodes in RMNP under specific meteorological conditions (e.g. upslope events) (Wolfe et al., 2003; Benedict et al., 2013). Source apportionment methods have aided in identifying and understanding those conditions (Gebhart et al., 2011), allowing meteorologists to predict when upslope events are likely to occur and thus the development of voluntary emission management strategies (Ndegwa et al., 2008) to mitigate Nr transport and deposition into RMNP during these periods.

For Nr species, the types of source apportionment models generally used are hybrid receptor models or source models. The hybrid receptor modeling techniques combine concentration observations made at a receptor location with transport-forecasting algorithms based on locally observed or regionally modeled meteorological data to limit the realm of possible model solutions (Prenni et al., 2014; Gebhart et al., 2011, 2014). Source modeling techniques follow the emitted pollutant from emission, through transport, transformation and removal in the atmosphere to estimate source impacts at a receptor location. Source models make the most use of detailed data (e.g. emissions source strength and location, meteorology, and atmospheric chemical and physical processes), but are computationally expensive. The most common examples of source models are CTMs (e.g., CAMx) designed with adjoint modules to monitor and track the transport and chemistry of the emissions of interest and output their contributions to primary and (in some cases) secondary pollutants at any stage and any location during the model run.

While there are many developments that have improved the accuracy of source apportionment modeling, research is still needed to 1) improve base model performance through improvements in input data and process parameterizations, 2) incorporate the state of the science of chemical and physical atmospheric processes into source apportionment modules, and 3) improve methods to quantify uncertainty associated with source apportionment modeling. Improvement of emissions inventories for Nr is a key knowledge gap, especially for NH_3 emissions from agricultural sources. More detail on the location, seasonality and timing of emissions and more specificity of emissions by animal facility type is needed. Improvement of model meteorological fields is also needed (also a need for CTMs in general), including more accurate representation of rain (location and amount), which is extremely important for wet deposition, and general improvement of meteorological predictions in complex terrain. Incorporation of uncertainty measures into source apportionment modeling represents an important longer-term objective.

3.4. Characterizing uncertainty in deposition budgets

Until methods for rigorously quantifying uncertainty in total deposition methods can be developed, aspects of uncertainty in deposition budgets can be informed by comparisons of CTMs and MMF procedures to each other and observations. An important consideration in such

comparisons is that the observations themselves contain error. For example, biases in CASTNET filter-based HNO_3 and NO_3^- measurements resulting from volatility have been well documented (Lavery et al., 2009), as have biases in NADP/NTN NH_4^+ concentrations in precipitation resulting from possible microbiological processes (Gilliland et al., 2002; Walker et al., 2012a). Implementation of standardized protocols to estimate and report uncertainty in network monitoring data is an important goal. Participation in interlaboratory comparison programs is also essential for maintaining comparability of data across networks (e.g., NADP, CASTNET, CAPMoN; Wetherbee et al., 2010).

Zhang et al. (2018a) recently conducted a study of long-term trends in wet deposition of inorganic N and S in the U.S., which included an evaluation of coupled WRF-CMAQ V5.0.2 (36 km resolution) against NTN measured annual wet deposition. Normalized mean bias (model – observation) was -32.1% for TNO_3 ($\text{NO}_3^- + \text{HNO}_3$) and -33.7% for NH_x ($\text{NH}_3 + \text{NH}_4^+$), evaluated across the CONUS, after adjusting for bias in precipitation amount at the monthly time scale. At finer grid resolution (12 km), evaluation of CMAQ V5.0.2 for the period 2002–2012 shows smaller biases of -0.7% and -10.2% for NO_3^- and NH_4^+ , respectively (Zhang et al., 2019). CMAQ tends to underestimate wet deposition, though performance tends to be better in the eastern U.S. owing to more complex terrain in the West. Makar et al. (2018) recently evaluated GEM-MACH V2 against annual measured wet deposition in Alberta and Saskatchewan, also noting an underestimate of modeled total $\text{NO}_3^- + \text{NH}_4^+$ deposition (slope = 0.89). Model biases relative to measured NTN annual wet deposition of -38% and -48% for NO_3^- and NH_4^+ , respectively, have been observed in evaluating CAMx V6.1 (12 km resolution) over the western U.S. (UNC/ENVIRON, 2015). Model performance may differ from these regional and continental assessments over smaller domains, particularly in complex terrain (Zhang et al., 2018b).

Multi-model comparisons have also been useful for assessing the variability of N deposition estimates. The variance of modeled total NO_y deposition was 10–30% across most of North America among the 23 models assessed in the PhotoComp study for the year 2000 (Dentener et al., 2006). Similar variance of 20–30% in wet and dry deposition of both NO_y (10 models) and NH_x (5 models), integrated over North America, was reported for the year 2000 in The Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP; Lamarque et al., 2013). In contrast, total deposition of NO_3^- in North America among 5 different models assessed in the Air Quality Model Evaluation International Initiative (AQMEII) had a variance of $>50\%$ (Solazzo et al., 2012; modeled year 2006). While more detailed analyses are ongoing, initial comparisons of the TDep and ADAGIO MMF procedures are promising. When total deposition is summed over the CONUS for the year 2010, the difference between methods is $<10\%$ (Walker et al., 2019b).

Downscaling deposition estimates from CTM grid cells to specific ecosystems is another important aspect of uncertainty in critical load assessments that is not directly informed by the model intercomparisons described above. Recent studies providing ecosystem specific model deposition estimates allow for assessment of the impact of downscaling. Schwede et al. (2018) examined deposition to global forests and contrasted grid-based with land use specific values from the co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (EMEP) model (Simpson et al., 2012), finding differences up to a factor of 2. Generally, the deposition velocity to a forest is higher than other land use types, primarily due to the higher leaf area and surface roughness. Paulot et al. (2018) found that grid-based results underestimated deposition to natural vegetation by up to 30% compared to downscaled deposition values in the National Oceanic and Atmospheric Administration (NOAA) Geophysical Fluid Dynamics Laboratory (GFDL) model.

Fig. 7 compares CMAQ V5.3 land use specific fluxes to grid cell average values, illustrating the differences that can be observed even at smaller grid sizes (12 km $\times$ 12 km). Grid average values are calculated

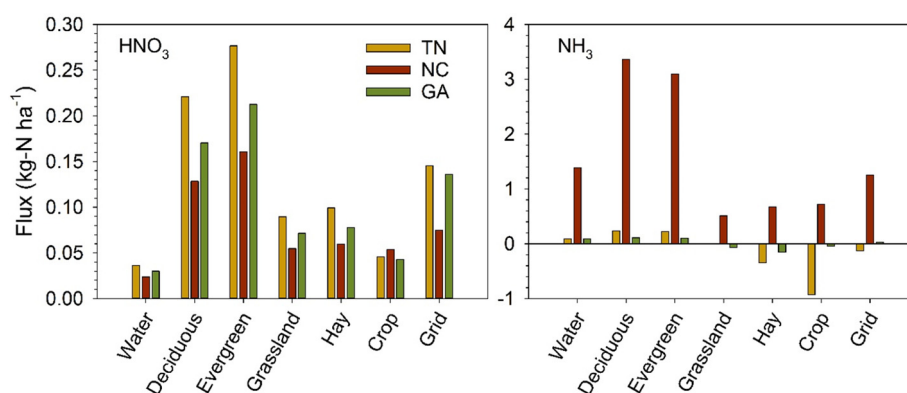


Fig. 7. CMAQ (V5.3 with STAGE) land use specific and grid average fluxes during July 2011 for three locations in Tennessee (TN), North Carolina (NC), and Georgia (GA) in the southeastern U.S. Positive fluxes indicate deposition.

using the Surface Tiled Aerosol and Gaseous Exchange (STAGE, Bash et al., 2018) module by summing the product of the land use specific flux and the fraction of the grid covered by that land use type. Consistent with the results of Schwede et al. (2018), large differences between grid average and land use specific fluxes can occur for HNO₃ over forests. Treatment of subgrid variations in land use is particularly challenging for bi-directional NH₃ fluxes. For example, differences in emission potentials and compensation points between natural ecosystems and fertilized crops result in differences in the direction and magnitude of land use specific fluxes within a grid cell (TN and GA in Fig. 7). In eastern North Carolina (Fig. 7), high atmospheric concentrations of NH₃ associated with CAFO emissions result in modeled net deposition (i.e., atmospheric NH₃ > surface compensation point) to all land use types within the grid cell, though much higher deposition occurs over forests compared to the grid value. Such analyses further highlight the need for land use specific deposition in CTM and MMF derived total deposition budgets used for ecosystem specific assessments.

Quantitative estimates of uncertainty in total Nr deposition are needed to assess uncertainty in critical load exceedances. Further comparisons of models (e.g., AQMEII Phase 4) and MMF procedures will aid in identifying and characterizing aspects of uncertainty in modeled Nr deposition estimates and in prioritizing model improvements. Approaches are also needed to rigorously quantify uncertainty in MMF derived total deposition. This will require development of methods for aggregating uncertainties in measurements, bias corrections in the fusion process, modeled variables, spatial interpolation and other aspects of MMF procedures. Until then, simpler metrics of deposition uncertainty may be useful to scientists and land managers (Walker et al., 2019b).

4. Enhanced coordination to address overarching research themes

The knowledge gaps outlined in the preceding sections impact a broad group of stakeholders, including federal and state agencies, academia, industry, and non-profit groups. Within the more specific topics identified, there are several overarching research themes that span across the needs of stakeholder groups and represent opportunities for enhanced coordination to more rapidly advance deposition science. Improving current understanding of the linkages between agricultural emissions and Nr deposition and better characterization of spatial and temporal patterns and trends in Nr deposition are two examples discussed in the following sections.

4.1. Improved understanding of the linkages between agricultural emissions and Nr deposition

The need to better understand linkages between agricultural emissions and Nr deposition is a theme that appears in many of the

knowledge and data gaps described in Section 3. Fig. 8 illustrates some of the science and policy issues encompassed by this broad research theme and examples of their relevant stakeholders. Examples of science needs include:

- improved estimates of NH₃ emissions from agricultural sources for modeling of air quality, visibility, and Nr deposition
- better understanding of the contribution of NH₃ to total Nr deposition to land and water
- more accurate apportionment of sources of Nr deposition.

Examples of policy issues underlying these science needs include:

- linking atmospheric Nr levels and speciation to deposition rates for specific ecosystems
- quantifying critical loads and their exceedances
- determining the source(s) of Nr deposition in ecosystems experiencing exceedances
- evaluating the effectiveness of existing policies for managing Nr emissions.

U.S. federal agencies share interconnected scientific and policy interests in agricultural emissions and linkages to Nr deposition. For example, EPA, NPS, NOAA, National Aeronautics and Space Administration (NASA), and National Science Foundation (NSF) have a shared interest in better understanding atmospheric chemistry to inform air quality, visibility, and earth system processes. Programs within the USDA Agricultural Research Service (ARS) and USDA National Institute of Food and Agriculture (NIFA) address aspects of measurement and modeling of NH₃ emissions from fertilized soils and animal production and local-scale or “near-field” deposition of NH₃. The USDA Natural Resources Conservation Service (NRCS) has an interest in developing and evaluating best management practices (BMPs) to reduce agricultural emissions that can impact protected lands. USGS and NOAA have an interest in understanding the contributions of agricultural sources of Nr to impaired waters and impacts in aquatic ecosystems.

Land management agencies (i.e., NPS, USDA, U.S. Forest Service (FS), Bureau of Land Management (BLM), U.S. Fish and Wildlife Service (FWS)) need speciated total Nr deposition estimates to assess critical loads. Establishment of a critical Nr load for RMNP and a goal of reducing N deposition over time (CDPHE, 2007) has brought together a range of stakeholders including the NPS, EPA, the state of Colorado, and Colorado agricultural producers. The producers have a stake in exploring ways to improve emissions estimates and developing cost effective BMPs. Collectively, the science underpinning the improvement of total Nr deposition budgets benefits the larger critical loads community. Enhanced coordination across the stakeholder groups in Fig. 8 would facilitate more rapid progress in implementing research needed to better

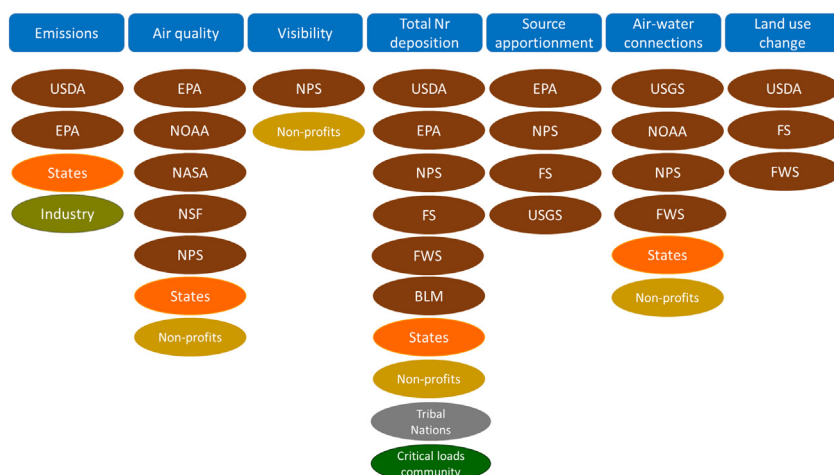


Fig. 8. Schematic showing the science and policy issues associated with the “Linkage between agricultural emissions and Nr deposition” (top row) and examples of stakeholders (ovals). Figure is intended as an example and is not a comprehensive list of stakeholders or the interests of the stakeholders included.

understand the role of agriculture in Nr deposition at the U.S. national scale.

4.2. Better characterization of patterns and trends in Nr deposition

Monitoring networks are a cornerstone for developing the information needed to characterize and address Nr deposition issues. Nr science is grounded in several key monitoring programs including NADP and CASTNET. However, current network designs have a number of gaps. For example, these networks were designed to assess the effectiveness of programs to reduce emissions from Electrical Generation Units (EGU) at regionally representative rural locations. Given the extent of NO_x emission reductions and the increasing need to better understand Nr from other sources (e.g., agricultural) and in other environments (e.g., urban), additional routine monitoring is needed.

Urban areas represent a key geographical gap with respect to Nr deposition where “hotspots” have been observed but atmospheric Nr contributions to urban water quality remain poorly understood. Enhanced stakeholder collaboration to expand NADP/NTN monitoring for urban environments could build on current federal and state air (see Appendix A) and water monitoring efforts (e.g., USGS). The urban deposition monitoring gap is of interest to multiple stakeholders, including federal agencies (EPA, USGS), states, and non-profit groups (e.g., Chesapeake Bay Foundation) with respect to understanding the sources of Nr impacting water quality and Total Maximum Daily Loads (TMDLs). For example, proper apportionment of sources of Nr to aquatic resources is of interest to EPA, while knowledge of urban sources of N pollution that ultimately impact water quality in estuaries and coastal zones is of interest to NOAA. Increased coordination of deposition and water quality monitoring would provide natural resource managers with better information to apportion sources of pollution, understand and anticipate trends, and assess benefits of BMPs, pollution control technologies, infrastructure upgrades, and environmental policies (Amos et al., 2018).

Enhanced monitoring is also needed to better characterize spatial and temporal patterns of NH₃ and NH₄⁺ in air and precipitation. Expansion of AMoN in agricultural areas would address a monitoring need to better characterize trends and patterns in air concentrations of NH₃ that would inform several of the science and policy issues illustrated in Fig. 8. Collaboration among NADP, USDA, and State Agricultural Experiment Stations could be explored, as well as opportunities to coordinate new air monitoring sites with water monitoring infrastructure (e.g., states, USGS) to inform air-water linkages in agricultural regions (Amos et al., 2018). Expanding AMoN is an opportunity to advance NH₃ dry

deposition modeling through collaboration between NADP and ecological networks such as Ameriflux, NSF Long Term Ecological Research (LTER) sites (<https://lternet.edu/about/>), and the National Ecological Observatory Network (NEON, <https://www.neonscience.org/>). Micro-meteorological and biogeochemical data collected by these networks would be useful for modeling NH₃ dry deposition.

Inclusion of NO₂ and organic forms of Nr in routine Nr deposition monitoring is also needed. Organic forms of Nr are not currently measured in national monitoring networks and NO₂ is primarily measured in urban areas (see Appendix A). Adaptation of NTN methods to include bulk water-soluble ON in wet deposition would be an important step toward more complete estimates of total Nr deposition and represents an opportunity for collaboration between North American wet deposition networks (NADP, CAPMoN, Mexico) to evaluate and standardize appropriate methods for routine measurements. Characterization of the spatial variability of NO₂ by remote sensing to inform expanded ground-based monitoring for deposition applications represents an opportunity for enhanced coordination between NASA and existing networks such as CASTNET.

The various government agencies and other stakeholders listed in Fig. 8 are already working together on Nr deposition issues in many cases. However, enhanced coordination is needed to more rapidly address the most pressing data and knowledge gaps limiting further development of Nr deposition budgets in the U.S.

5. From deposition to ecosystem response

In this article, we summarize the state of the science of Nr deposition budgets in the U.S. and address areas where research is needed to improve measurements and models of deposition, reduce uncertainties in critical load exceedances, and more accurately determine the sources of Nr deposition. Outcomes of this research will inform the scientific basis for evaluating the effectiveness of policies for managing Nr pollution, including the secondary NAAQS and critical loads, water quality impairment, and agricultural sources.

As the deposition science community in North America moves forward on the research needs documented here, we encourage engaging with biogeochemical and ecological communities studying ecosystem exposure and response. For example, as the representation of biogeochemical processes in deposition models becomes more mechanistically complete and the computational expense of running fully coupled air-water-land models is reduced, exposure and ecophysiology may be more explicitly linked. Thus, it becomes easier to quantitatively relate Nr deposition and ecosystem response within the context of other

drivers of ecosystem change (e.g., climate, air quality, land cover). Closer collaboration between deposition scientists and ecologists could better inform the science of deposition–ecosystem linkages and identify and prioritize the measurements needed for model development and evaluation.

Appendix A

Table A1

Existing North American monitoring networks that measure components of Nr in the atmosphere or precipitation (wet deposition).

Network	Reactive nitrogen measurements	Measurement interval	Website
Canadian Air and Precipitation Monitoring Network (CAPMoN)	Ambient concentrations of NH_4^+ , NO_3^- , HNO_3 ; Concentrations of NO_3^- and NH_4^+ in precipitation; precipitation amounts	Daily	https://www.canada.ca/en/environment-climate-change/services/air-pollution/monitoring-networks-data/canadian-air-precipitation.html
Chemical Speciation Network (CSN)	Ambient concentrations of NO_3^- , NH_4^+	Daily (1:3 or 1:6 day)	https://www3.epa.gov/ttn/amtic/speciepg.html
Clean Air Status and Trends Network (CASTNET)	Ambient concentrations of NH_4^+ , NO_3^- , HNO_3	Weekly	https://epa.gov/castnet
Interagency Monitoring of Protected Visual Environments (IMPROVE)	Ambient concentrations of NO_3^- , particulate nitrite (NO_2^-)	Daily (1:3 day)	http://vista.cira.coloradostate.edu/improve
NADP's Ammonia Monitoring Network (AMoN)	Ambient concentrations of NH_3	Bi-weekly	http://nadp.slh.wisc.edu/AMoN/
NADP's Atmospheric Integrated Research Monitoring Network (AIRMoN)	Concentrations of NO_3^- and NH_4^+ in precipitation; precipitation amounts	Daily	http://nadp.slh.wisc.edu/AIRMoN/
National Atmospheric Deposition Program (NADP) National Trends Network (NTN)	Concentrations of NO_3^- and NH_4^+ in precipitation; precipitation amounts	Weekly	http://nadp.slh.wisc.edu/NTN/
National Core (NCore) Multipollutant Network; State and Local Air Monitoring Stations (SLAMS); National Air Monitoring Stations (NAMS)	Concentrations of NO , NO_2 , NO_x , total oxidized nitrogen (NO_y); PM speciation (CSN or IMPROVE)	Hourly	https://www3.epa.gov/ttn/amtic/ncore ; https://www3.epa.gov/airquality/montrng.html
Canada's National Air Pollution Surveillance Program (NAPS)	Concentrations of NO , NO_2	Hourly	https://www.canada.ca/en/environment-climate-change/services/air-pollution/monitoring-networks-data/national-air-pollution-program.html
Near-road NO_2 Monitoring	Concentrations of NO_2	Hourly	https://www3.epa.gov/ttnamti1/nearroad.html
Photochemical Assessment Monitoring Stations (PAMS)	Concentrations of NO , NO_2 , NO_y , NO_x	Hourly	https://www3.epa.gov/ttn/amtic/pamsmain.html

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6. Disclaimer

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