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Aspects of uncertainty in total reactive nitrogen deposition estimates for North American critical load applications

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Abstract

Determination of the amount of reactive nitrogen (Nr) deposition in excess of the ecosystem critical load (CL) requires an estimate of total deposition. Because the CL exceedance is used to inform policy decisions, uncertainty in both the CL and the exceedance itself must be understood. In this paper we review the state of the science with respect to the sources of uncertainty in total Nr deposition budgets used for CLs assessments in North America and put forth recommendations for research and monitoring to improve deposition measurements and models. In the absence of methods to rigorously quantify uncertainty in total Nr deposition, a simple weighted deposition uncertainty metric (WDUM) is introduced as a tool for scientists and decision makers to use in assessing CL exceedances. Maps of the WDUM applied to National Atmospheric Deposition Program (NADP) Total Deposition (TDep) estimates show greater uncertainty in areas of the U.S. where dry deposition makes a larger contribution to the deposition budget, particularly ammonia (NH3) in agricultural areas and oxidized nitrogen (NOx) in urban areas. Organic N deposition is an important source of uncertainty over much of the U.S. Our analysis illustrates how the WDUM can be used to assess spatial patterns of deposition uncertainty and inform actions to improve deposition budgets for CL assessments at the local scale.

1 Introduction

Reactive nitrogen (Nr) additions can lead to detrimental effects in terrestrial and aquatic ecosystems through a combination of eutrophication and acidification responses. As awareness of these impacts increased in the mid-to-late 20th century, the Clean Air Act and subsequent amendments were passed to reduce Nr emissions and their impact to human health and the environment in the U.S. Additionally, because Nr can be transported across borders, Nr deposition is included in agreements such as the International Convention on

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Long-Range Transboundary Air Pollution and the U.S.-Canada Air Quality Agreement. These policies rely on accurate estimates of Nr deposition from direct measurements, models, and manipulation of background deposition through fertilization to understand how much Nr leads to an ecosystem change.

The *"quantitative estimate of an exposure … below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge"* is known as the critical load (CL) (Nilsson and Grennfelt, 1988). CLs have been developed in the U.S. for a range of ecosystem impacts including terrestrial and aquatic acidification, forest-tree health, NO_3^- leaching, changes in plant community composition, and changes in lichen communities (Clark et al., 2018). Exceedance of the CL occurs when the amount of Nr deposited is greater than the threshold designated for change to occur. The uncertainty of both the Nr deposition estimates and ecosystem responses need to be understood to evaluate risk to the ecosystem. Consideration of uncertainty in determining whether a CL is used in a management or policy response is currently based on an assessment of reliability (Bobbink et al., 2003; Pardo et al., 2011). CLs are categorized as Reliable (highest confidence), Fairly Reliable, or Expert Judgement (lowest confidence) based on the number and comparability of studies in which a particular ecosystem response was determined. An estimate of uncertainty in the deposition amount is specifically needed to assess uncertainty in the CL exceedance and would also facilitate a more direct consideration of deposition as a component of uncertainty in the CL itself.

Estimates of Nr deposition used in North American ecosystem assessments are typically derived from chemical transport models (CTMs) (Ellis et al., 2013; Lee et al., 2016; Simkin et al., 2016; Clark et al., 2018; Makar et al., 2018) or by measurement-model fusion (MMF) techniques (Schwede and Lear, 2014; Nanus et al., 2017; McDonnell et al., 2018; U.S. EPA, 2019). CTMs must accurately simulate the fundamental processes that govern the composition of the atmosphere, including emissions, transport, chemical transformations, and ultimately wet and dry deposition. Though the underlying fusion procedures and spatial interpolations contain some error, MMF estimates of deposition are considered more accurate than CTMs due to incorporation of measurement data. In addition to uncertainties in the deposition estimates themselves, downscaling from CTM grids to specific ecosystems is another important source of uncertainty in CL assessments (Paulot et al., 2018; Schwede et al., 2018).

While some aspects of these uncertainties have been quantified in the context of CL exceedances (Williams et al., 2017), estimates of the total uncertainty of CTM and MMF derived total deposition budgets are not yet available. These deposition budgets are often accepted as the best data available for predicting ecosystem risk and are subsequently applied without an accompanying estimate of uncertainty. However, knowledge of uncertainty in the deposition estimate is important because it can help to inform whether a policy or management action is warranted. Figure 1 uses data for the CL for a decrease in species richness with increasing Nr to illustrate how uncertainty in deposition estimates may influence whether or not a CL is exceeded (Simkin et al., 2016). In this example, 12.4% of all locations are within ± 2 kg ha^{-1} yr^{-1} of exceedance (red, orange, yellow, and green points in Figure 1) when compared to total Nr deposition estimated using the National Atmospheric

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Deposition Program (NADP) Total Deposition (TDep) MMF approach (Schwede and Lear, 2014). Negative values indicate “near-exceedance” sites that are not currently assumed to be at risk but would be if deposition is underpredicted (i.e., yellow and green points). Alternatively, positive values indicate sites currently deemed at risk that would not be if deposition were overestimated (i.e. orange and red points). The wide range of deposition (6 −16 kg ha^{-1} yr^{-1}) in which these near-exceedances occur highlights that resolving uncertainty is important at both high and low levels of deposition.

The potential of misunderstanding exceedances has policy and management implications regarding the perceived risk to ecosystems from current and future deposition. During the New Source Review process (U.S. Forest Service., 2011), Class I national parks and wilderness areas are assessed for potential adverse effects from new emissions. If deposition is over or under predicted, then the assessment for the Prevention of Significant Deterioration may be inaccurate (U.S. Forest Service., 2011). Additionally, land managers use exceedances to develop resource management strategies to achieve CLs. Knowledge of whether the uncertainty of the exceedance is considered low or high can increase the effectiveness of policy, planning, and permit review and inform the level of confidence with which actions can be taken. For example, at a location where the CL exceedance is large and uncertainty in the deposition estimate is considered low, a land manager may be more confident that implementing a strategy to meet the CL is appropriate and will be effective. Conversely, knowledge that deposition at a near-exceedance location is considered highly uncertain would be beneficial in developing research and monitoring strategies to improve deposition estimates and reduce uncertainties so that a policy for achieving the CL could be more confidently implemented in the future. Knowledge of the relative uncertainties of the components of the Nr deposition budget would help prioritize research and monitoring to address the most important and uncertain species, processes, and pathways (i.e., wet versus dry). Until rigorous quantitative estimates of uncertainty in total deposition are available, a simpler metric of uncertainty would be helpful for assessment of CL exceedances.

In this paper we briefly review the state of the science with respect to the sources of uncertainty in total Nr deposition budgets used for CL assessments. In the absence of methods to quantify these cumulative uncertainties in an absolute sense, a simple uncertainty metric for total Nr deposition is introduced. This metric is used to illustrate how understanding uncertainty in total Nr deposition budgets will assist in prioritizing future research and facilitate more informed management decisions. We then outline several recommendations for data synthesis, new measurements, and comparisons and improvements to models that will improve the accuracy and spatial representativeness of Nr deposition budgets and allow more rigorous estimates of uncertainty in the future.

2 Measurements and modeling platforms used in North American Nr deposition budgets

2.1 Measurement networks

The key monitoring networks supporting North American Nr deposition assessments (Supplemental Figure S1) are the NADP/National Trends Network (NTN), NADP/

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Atmospheric Integrated Research Monitoring Network (AIRMoN), the Clean Air Status and Trends Network (CASTNET) and the Canadian Air and Precipitation Monitoring Network (CAPMoN). The NADP/NTN network (http://nadp.slh.wisc.edu/NTN/) spans the contiguous US (CONUS) and extends into Canada, Puerto Rico, Mexico, and Alaska. It currently has 257 sites and the program dates back to 1978. The sites collect wet-only deposition samples and aggregate precipitation totals. The samples are collected weekly and sent to the NADP central analytical laboratory for analysis of dissolved inorganic N (NH_4^+ and NO_3^-), along with sulfate, chloride, bromide, and base cations. The NADP/AIRMoN network (http://nadp.slh.wisc.edu/AIRMoN/) includes 7 sites and has been operating since 1992. These sites collect daily wet-only deposition samples that are also analyzed at the NADP laboratory. The precipitation-chemistry component of the CAPMoN (https://www.canada.ca/en/environment-climate-change/services/air-pollution/monitoring-networks-data/canadian-air-precipitation.html) network provides daily wet-only samples of dissolved inorganic N concentrations in precipitation, along with sulfate, chloride, and base cations. The network currently has 29 sites and dates back to 1983.

CASTNET (https://www.epa.gov/castnet) and CAPMoN both collect integrated ambient air concentrations of gases and particles using an open-face filterpack. The same arrangement of filters are used in both CAPMoN and CASTNET, but CASTNET filters are exposed for a week-long period at low flow rates (1.5 and 3.0 L min^{-1} for Eastern and Western sites, respectively) while CAPMoN uses a higher flow rate (17.5 L min^{-1}) and 24-h collection. There is no explicit particle size cut in either network, thus fine and coarse mode particles are collected. CASTNET currently comprises 95 rural sites dating back to 1988. CAPMoN, in addition to the precipitation chemistry sites mentioned above, operates 18 ambient air sites dating back to 1983. Other air monitoring networks measuring atmospheric Nr are briefly described in Supplemental Material (Section S1.1).

2.2 Modeling platforms

2.2.1 Chemical transport models—In North America, the Community Multi-scale Air Quality Model (CMAQ), Global Environmental Multiscale model – Modeling Air quality and CHemistry (GEM-MACH), and the Comprehensive Air Quality Model with Extensions (CAMx) are the primary regional CTMs used to provide gridded deposition for CLs and other deposition assessments. For example, CMAQ deposition values are used in the TDep MMF procedure (Schwede and Lear, 2014) and to assess long term trends in deposition over the U.S. (Zhang et al., 2018b). Wet and dry Nr deposition fluxes have been output from different versions of GEM-MACH, both across North America at a 10-km horizontal resolution (Moran et al., 2017) and in regional studies at higher resolution (Makar et al., 2018). GEM-MACH deposition is also used in the Atmospheric Deposition Analysis Generated by optimal Interpolation from Observations/Analyse du Dépôt Atmosphérique Généré par Interpolation optimale des Observations (ADAGIO) MMF procedure. The CAMx model has recently been used to examine the contribution of various sources to Nr deposition in the Greater Yellowstone area (Zhang et al., 2018a) and Rocky Mountain National Park (Thompson et al., 2015). Features of these models relevant to uncertainty in deposition assessments, including emissions, chemistry modules, land use, and deposition schemes, are briefly described in Supplemental Material (Section S1.2.1).

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2.2.2 Measurement-model fusion—In an effort to reduce uncertainties and biases associated with CTM predictions, MMF approaches are increasingly being used to estimate total Nr deposition (Schwede and Lear, 2014; Nanus et al., 2017; McDonnell et al., 2018; U.S. EPA, 2019; World Meteorological Organization, 2017). In MMF, CTM output is combined with wet deposition and air concentrations from network measurements. While the methods of combining the fields can be similar to those used in data assimilation, the model is not re-forecast from the adjusted fields as is typical for data assimilation applications. TDep and ADAGIO are two examples of MMF used in North America.

The TDep MMF approach (Supplemental Figure S2) combines spatially interpolated CASTNET monitoring data with CMAQ deposition velocities to estimate dry deposition of HNO_3, NO_3^-, and NH_4^+. The CASTNET monitoring data is also used to bias adjust the CMAQ dry deposition estimates as the measured data is considered more accurate and to avoid large step functions between the measured and modeled data. The measured and CMAQ modeled dry deposition datasets are combined based on inverse distance weighting (IDW) of the measured versus modeled value as a function of distance from the measurement location (Schwede and Lear, 2014). For Nr species not measured at CASTNET sites (i.e. gas phase NO, NO_2, HONO, N_2O_5, NH_3, PANs, organic nitrates), the CMAQ dry deposition estimates are used directly (uncorrected). NH_3 dry deposition is modeled using a bi-directional flux framework (Bash et al., 2013). NADP measurements of precipitation amount and chemistry are combined with estimates of precipitation amount from the Parameter-elevation Regressions on Independent Sloped Model (PRISM, Daly et al., 2008) to produce spatially interpolated NO_3^- and NH_4^+ wet deposition fields. Dry and wet deposition are combined to produce weekly gridded maps of total deposition of Nr for the CONUS at a 4-km resolution, which are aggregated to annual deposition. More detailed information on the TDep method is available in Schwede and Lear (2014) and at http://nadp.slh.wisc.edu/committees/tdep/tdepmaps/.

A slightly different approach has been developed by Environment and Climate Change Canada (ECCC). The ECCC project ADAGIO (Supplemental Figure S2) generates maps of optimized wet, dry and total annual deposition of N, sulphur (S), and ozone in Canada and the U.S. by combining observed and modelled data. For Nr, 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 techniques. Optimal interpolation is a statistical method for weighting model and measurements based on error covariance parameters assigned to each data source to represent model and measurement uncertainty (Robichaud and Menard, 2014). 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. Wet and dry deposition fluxes of unmeasured species, including N_2O_5, HONO, and organic nitrates, are taken from the model directly.

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3 Aspects of uncertainty in Nr deposition budgets

CL exceedances may be calculated using the variety of deposition measurements and models described above. For deposition and CLs to be effectively combined for policy or management action, understanding of the relevant uncertainties and limitations in both components is needed.

3.1 Completeness of the budget

North American monitoring networks that support deposition research characterize only inorganic species in wet deposition and concentrations of particles and gases in air; organic compounds are not routinely measured. Atmospheric organic N is highly diverse, originating from soil, biomass burning, agricultural, marine, and anthropogenic sources. Primary emissions and secondary reaction products include amines and amino acids, urea, nitrophenols, alkyl amides, N-heterocyclic alkaloids, and organic nitrates (Jickells et al., 2013; Cape et al., 2011). Globally, organic N compounds contribute ~ 25% of total water-soluble N in precipitation on average (Jickells et al., 2013), with a similar fraction observed in particulate matter (Cape et al., 2011). In the U.S, annual averages for rainfall and PM range from 2.6% to 33% of total N as ON (Scudlark et al., 1998; Keene at al., 2002; Whitall and Paerl, 2001; Beem et al., 2010; Benedict et al., 2012; Walker et al., 2012; Zhang et al., 2002a; Russell et al., 2003; Calderon et al., 2007; Lin et al., 2010; Zamora et al., 2011; Chen et al., 2018).

Representation of organic N in deposition budgets relies on model estimates. For the current TDep MMF, CMAQ Version 5.0.2 includes only peroxyacyl nitrate (PAN), aromatic PANs (OPAN), C3 and higher PANs (PANX), and some organic nitrates in the gas phase. Thus, the organic fraction of Nr dry deposition represents an underestimate. Wet deposition of organic N is also not well represented in CMAQ V5.0.2 due to a limited range of solubilities specified for organic nitrates. Subsequently, wet deposition of organic N is not included in the TDep Nr budget. In GEM-MACH, only PAN is treated individually, with an additional grouped “organic nitrates” species, and therefore is subject to similar limitations as CMAQ. Chemical mechanisms used with many CTMs are actively being updated to include more advanced treatment of organic N species (Luecken et al, 2019; Pye et al., 2015).

In the TDep maps, organic N dry deposition is included in the “non-measured other N” group with NO, NO_2, HONO, and N_2O_5. While NO and NO_2 are measured in urban and suburban networks (see Supplemental Material Section S1.1), these measurements are not currently included in the TDep fusion procedure. As predicted by CMAQ (V5.0.2), dry deposition of “other N” contributes an average of ~ 13% of the total deposition budget over the CONUS. Larger contributions are observed in urban areas of eastern U.S. where dry deposition of NO_2 associated with mobile NOx sources is important. These patterns of oxidized Nr deposition underscore the need for incorporation of NO2 measurements from urban and suburban networks into the TDep MMF and new measurements of NO2 concentrations and fluxes to better characterize deposition along urban to rural gradients. The latter may be complemented by the use of satellite observations to characterize spatial patterns (Cheng et al., 2013). In addition to underrepresentation of the dry organic N deposition, the mobile NOx emission inventory, which may be biased high (~ 30%,

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McDonald et al., 2018), is another potentially important source of uncertainty in TDep estimates of "other N" dry deposition.

3.2 Characterizing uncertainty and bias in deposition estimates

3.2.1 Measurement to model comparisons—Biases in modeled deposition rates can be assessed by direct comparisons of measured versus modeled wet and dry deposition as well as the components of the deposition calculation. For wet deposition, the latter would include comparison of measured versus modeled precipitation amount, which is needed to calculate wet deposition. An evaluation of dry deposition could be informed by comparison of measured versus modeled air concentrations, which are applied to deposition velocities to calculate dry deposition rates.

It is important to note that the measurements used to directly calculate deposition, bias correct modeled air concentrations, and evaluate model performance contain error themselves. For example, Wetherbee et al. (2005) report median absolute errors of 11.3% and 4.97% for NTN measurements of NH_4^+ and NO_3^- concentrations in precipitation, respectively, for collocated AeroChem Metrics Model 301 collectors. Studies show that concentrations of NH_4^+ in NTN precipitation samples are biased low ~ 10%, potentially due to microbiological processes (Gilliland et al., 2002 and references therein; Walker et al., 2012). Sickles and Shadwick (2002) report median absolute relative differences for paired observations of CASTNET measured NH_4^+, HNO_3, and NO_3^- air concentrations of 3.0, 5.5, and 7.8%, respectively. The filter-based methods employed by CASTNET and CAPMoN have been shown to exhibit biases in NO_3^- (low) and HNO_3 (high) associated with volatility of NH_4NO_3 aerosol (Lavery et al., 2009; Zhang et al, 2009), though the total NO_3^- (gas + aerosol) is generally conserved (Lavery et al., 2009). It is noted that these studies have generally focused on NO_3^- sampling biases (see Lavery et al., 2009 and references therein), rather than NH_4^+. Regarding volatility, bias in fine mode NH_4^+ should be lower in areas where NH_4^+ is primarily associated with sulfate. Aspects of variability and bias associated with analytical procedures employed by the NADP, CASTNET, and CAPMoN networks are assessed through interlaboratory comparison programs (Wetherbee et al., 2010). These uncertainties and biases should be considered in comparisons of models to observations.

Zhang et al. (2018b) recently conducted a study of long-term trends (1990–2010) in wet deposition of inorganic N in the U.S., which included an evaluation of coupled WRF-CMAQ V5.0.2 (36 km resolution) against NTN measured annual wet deposition. Evaluated across the entire CONUS, normalized mean bias (model – observation) was −32.1% for TNO_3 (NO_3^- + HNO_3) and −33.7% for NH_x (NH_3 + NH_4^+) after adjusting for bias in precipitation amount. Evaluation of CMAQ V5.0.2 at finer grid resolution (12 km) 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). Performance tends to be better in the eastern U.S. owing to more complex terrain in the West (Zhang et al., 2018b). In both studies, uncertainties in NH_3 emissions from agricultural sources and bidirectional NH_3 air surface exchange processes were noted as potential reasons for model underestimation. Makar et al. (2018) recently evaluated GEM-MACH V2 against annual measured wet deposition in an evaluation of CL exceedances in Alberta and Saskatchewan, also noting an underestimate of modeled total

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NO_3^- + NH_4^+ deposition (slope = 0.89). Evaluation of CAMx V6.1 (12 km resolution) over the western U.S. (UNC/ENVIRON, 2015) showed model underestimation of inorganic N wet deposition as well, with biases relative to annual measured NTN deposition of −38% and −48% for NO_3^- and NH_4^+, respectively. Over smaller domains in complex terrain, model performance may differ from regional and continental comparisons. For example, Zhang et al. (2018b) found positive biases of 31% and 49% in CAMx (12 km) estimates of NO_3^- and NH_4^+ annual wet deposition, respectively, compared to NTN in the Greater Yellowstone Area. Positive bias in precipitation amount was identified as an important contributor to the bias in wet deposition.

Evaluation against wet deposition measurements has also been performed in several multi-model comparison studies, including PhotoComp, Atmospheric Chemistry and Climate Model Intercomparison (ACCMIP), and Task Force Hemispheric Transport of Pollution (HTAP I and II) (see Tan et al., 2018). Typically, measurement data were compared with the multi-model mean. When comparing annual wet deposition of NO_3^- and NH_4^+ with NADP measured values, the mean of the models was mostly within 10–20% of measurements as shown by the slope of the model vs. measurement linear fit (Table 1) and the reported mean biases of 11–38% for NO_3^- and < 8% for NH_4^+ (summarized by Tan et al., 2018). While individual models may perform better for specific locations and/or chemical species, in general, the ensemble of the models is the most robust estimator of wet deposition when considering all species and regions (Dentener et al., 2006; Tan et al., 2018). Generalizing results from the studies summarized in Table 1, measurement-model differences are ~ 30% for wet deposition among the models investigated. Knowledge of precipitation amount is a key uncertainty in CTM predictions of wet deposition and calculations of wet deposition from measured precipitation chemistry (see Supplemental Material Section S2.1.1).

The dry component of Nr deposition is not directly measured in a routine monitoring mode in North America. Additionally, with exception of the work of Munger et al. (1996) at Harvard Forest, dry deposition measurements in North America typically only span weeks to a few months. While useful for examining deposition processes, these datasets are not sufficient in temporal coverage to characterize annual dry deposition budgets. A lack of speciated Nr dry deposition measurements precludes a rigorous evaluation of uncertainty in model deposition velocities and fluxes at the national scale (Zhang et al., 2002b; Walker et al., 2019). However, uncertainty in dry deposition can be partly informed by comparison of modeled and measured air concentrations (CMAQ, Appel et al., 2011; Appel et al., 2018; Zhang et al., 2018a; GEM-MACH, Makar et al., 2018; Moran et al., 2017; CAMx, Zhang et al., 2018b; UNC/Environ, 2015). Comparing CMAQ V5.2.1 (12 km) versus CASTNET weekly measured HNO_3, NO_3^-, NH_3, and NH_4^+ concentrations across the CONUS (Supplemental Figure S3), normalized median bias (model – observation) ranges from +25% for HNO3 to −27% for NH_3. Other studies have documented an underestimation of NH_3 air concentrations in CTMs compared to observations, noting incorrect magnitude (i.e., low) and spatial allocation of emissions, model grid resolution, and uncertainty in bidirectional exchange processes as reasons for disagreement (Kelly et al., 2014; Butler et al., 2015; Battye et al., 2016; Zhang et al., 2018b). The overestimate in HNO_3 may be related to uncertainties in emissions or representation of chemistry (Luecken et al., 2019). In Figure S3, a significant portion of the total root mean square error is unsystematic, reflecting

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differences between model and observations related to random processes. In the absence of bias correction, both components of error in the air concentration propagate to the model deposition calculation.

While data from routine networks are most commonly used in comparisons of measured versus modeled deposition, throughfall and bulk deposition measurements collected within smaller scale, more intensive studies are also used (see Supplemental Material Section S2.1.2).

3.2.2 Model to model comparisons—Models vary widely in their emissions inputs, horizontal and vertical resolution, and the chemical and physical processes represented. Multi-model comparisons can provide an overall estimate of the resulting variability in model outputs. A number of global- and continental-scale model intercomparison projects have assessed N deposition among other air quality outputs (Tan et al., 2018).

In the PhotoComp study for the year 2000 (Dentener et al., 2006), the variance of modeled NO_y wet deposition between the 23 models assessed was 10–30% across most of North America. While a corresponding spatial breakdown was not shown for NH_x deposition (reported by only 7 models), the variance was similarly reported to be about 30% in the anthropogenic emissions regions including North America. ACCMIP reported similar variance between models of 20–30% in wet and dry deposition of both NO_y (10 models) and NH_x (5 models) for the year 2000, integrated over North America (Lamarque et al., 2013). In contrast, in the Air Quality Model Evaluation International Initiative (AQMEII) study which modeled 2006, the estimated total deposition of NO_3^- in North America from 5 different models had a variance of more than 50% (Solazzo et al., 2012). However, in that case, the emissions used by each model were not identical.

CTM predictions of dry N deposition (oxidized and reduced) were also compared with site specific inferential model values based on air concentrations at CASTNET sites in a limited number of studies (Vet et al., 2014; Tan et al., 2018). When species such as NO_2 and NH_3 (not measured at CASTNET sites) are included in the modeled dry deposition, the model was higher than the inferential values by about a factor of 3 (Vet et al., 2014). However, excluding NO_2 and NH_3 dry deposition from the model totals in another study left the model dry N deposition values still higher by a factor of 2 compared to CASTNET inferential estimates (Tan et al., 2018). Further investigation of the comparisons revealed that it was primarily the air concentrations of HNO_3, particle NO_3^-, and particle NH_4^+ that were overestimated in the model compared to the CASTNET measurements, rather than significant differences in the dry deposition velocities. Some of this discrepancy may be due to the coarse resolution of many global models (Tan et al., 2018) or limitations in the representativeness of CASTNET sampling locations (Hicks et al., 2006). Such studies illustrate the large uncertainties in modeled dry deposition.

Nr species exhibit a range of physical and chemical properties, leading to very different behaviors in the dry deposition process, which is often modeled as a deposition velocity (V_d):

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$$V_d = 1/(R_a + R_b + R_c) \quad (1)$$

where R_a is the aerodynamic resistance to turbulent transfer from the atmosphere to the surface, R_b is the resistance to diffusion across the laminar boundary layer of air immediately above the receptor, and R_c is a resistance to uptake at the receptor surface, termed the canopy resistance. Wu et al. (2018) recently intercompared five dry deposition algorithms and found that the four models based on Monin-Obukhov similarity theory produced similar (± 20%) results for R_a and R_b.

Surface uptake, represented by R_c, may occur via stomatal and non-stomatal (e.g., ground, leaf cuticle, woody material) pathways. For Nr other than highly soluble species such as HNO_3 and N_2O_5, R_c is typically the largest resistance and thus controls V_d. Flux uptake by non-stomatal pathways cannot be measured directly or easily segregated from canopy scale flux measurements. For this reason, non-stomatal deposition processes remain poorly understood and therefore highly parameterized and uncertain, often producing large differences in modeled V_d (Wu et al., 2012). Adoption of a bidirectional flux framework for NH_3 (Flechard et al., 2013) which is now common in CTMs, requires the use of compensation point parameterizations (e.g., soil and vegetation emission potentials) that remain poorly characterized for many ecosystems, leading to large uncertainty in NH_3 dry deposition rates at the local scale (Dennis et al., 2013). Parameterization of emission potentials and surface resistances for NH_3 are largely derived from European experiments (Massad et al., 2010; Zhang et al., 2010) and their applicability to North American ecosystems remains an open question.

Recent assessments in Europe (Flechard et al., 2011) and the U.S. (Schwede et al., 2011; Li et al., 2016) show that commonly used inferential dry deposition models may differ by a factor of 3 or more in mean deposition (exchange) velocities of Nr species, despite being driven by the same on-site meteorology and parameters for site characterization (e.g. leaf area index, surface roughness length, canopy height, etc.). The most extensive comparison of dry deposition schemes for Nr was conducted by Flechard et al. (2011), in which four models used in CTMs and monitoring networks in Europe and North America were compared using measurements of micrometeorology, air concentrations, and surface characteristics at 55 sites within the NitroEurope network. Site-specific annual average fluxes reported in Flechard et al. (2011, Table 3) are summarized here in Table 2. Deviation among models is generally small for HNO_3, with the mean of the relative standard deviation of model fluxes at individual sites varying from 7% at grassland sites (N = 8) to 28% at forest sites (N = 29). Models diverged the most for NH_3, with the mean of the relative standard deviation of model fluxes at individual sites varying from 190% at grassland sites (N = 8) to 50% at forest sites (N = 29). For NH_3, parameterizations of non-stomatal resistances (e.g., cuticular) were identified as the main source of inter-model discrepancy. Summing model fluxes of the individual species, relative standard deviation of total N fluxes at individual sites varied from 37% over semi-natural vegetation (N = 9) to 67% at grassland sites (N = 29).

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3.2.3 Measurement-model fusion—There are several sources of uncertainty in MMF estimates of deposition including the observational data, the choice of CTM, and the fusion approach. Observational data may be spatially and temporally incomplete or inconsistent, depending on the networks used in the MMF. Spatial gaps in monitoring data can, for example, create artifacts in bias surfaces used to correct CTM output for dry deposition. Temporal gaps in data, which can be an issue at high elevation sites where wet deposition data may more frequently fail quality assurance requirements (Latysh and Wetherbee, 2012), can create inconsistencies in deposition time series. Temporal and spatial inconsistencies in MMF surfaces can also result in transitioning from measurement- to model-derived estimates when sites are shut down or change locations. Finally, observed values are not available for all chemicals. Subsequently, some important model species like organic N are not bias corrected in the MMF methods. The bias correction for measured species compromises the mass balance of the modeled deposition estimates. With the modeled concentrations of the other non-measured N species left uncorrected, the total amount of N deposited in the domain will be different than if the mass balance was maintained. However, previous work shows that the overall impact should be small (Dennis and Foley, 2009; Lear and Schwede, 2012). As further described in Supplemental Material, incommensurability (Section S2.2.1) of comparing model-grid average and pointwise observations (Swall and Foley, 2009) and the temporal consistency (Section S2.2.1) of MMF datasets can also represent sources of uncertainty.

MMF procedures can differ in the use of monitoring data, the treatment of deposition processes and the fusion procedure. For example, while ADAGIO uses NADP/AMoN NH_3 measurements in the fusion procedure, TDep does not. One reason is related to the high spatial variability of NH_3 concentrations, particularly in agricultural regions, which creates uncertainties in the IDW procedure for the TDep spatial interpolation (Schwede and Lear, 2014). These uncertainties could be reduced by expanding NH_3 monitoring in agricultural areas to better characterize spatial patterns in relation to sources. Enhanced ground-based monitoring could potentially be complemented with satellite observations of NH_3 (Kharol et al., 2018). As previously noted, TDep does not use measurements of NO_2 and other Nr species measured in urban and suburban networks while ADAGIO does, likely creating differences in estimates of deposition in these areas. Regarding differences in treatment of deposition processes, in contrast to CMAQ, the current version of GEM-MACH does not include bidirectional NH_3 flux. Another reason AMoN NH_3 measurements are not currently used in the TDep MMF relates to the challenges in bias correcting air concentrations in the compensation point based bidirectional flux model in CMAQ. Regarding wet deposition, TDep uses precipitation depth data from NADP and PRISM while ADAGIO uses data from CaPa. Differences in MMF deposition estimates may also arise from the fusion procedure itself. TDep uses IDW weighting of measured versus modeled values while ADAGIO uses optimal interpolation.

As shown in Figure 3 for 2010, over the contiguous U.S., 75% of the gridded TDep and ADAGIO values are within ±30%. When deposition is summed over the entire domain, the difference is less than 10%, with less total N deposition estimated by ADAGIO. Overall agreement is reassuring, given the many differences between the approaches, though regions

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with significantly larger differences exist. While a more detailed analysis is forthcoming, areas with high NH_3 concentrations appear to have larger differences, likely due to the bidirectional treatment in CMAQ (TDep) but not in GEM-MACH (ADAGIO).

3.3 Spatial representativeness

Typical dry deposition output from CTMs is provided at the grid scale and is obtained by averaging sub-grid variability in either surface characteristics or dry deposition velocities. The CTM does not spatially resolve the land use types within the model grid and only has knowledge of the percent coverage of the land use type. Differences in leaf area index (LAI), surface roughness, soil moisture, and plant stomatal response are some of the factors that contribute to sub-grid variability in V_d. For fast deposition species such as HNO_3, greater roughness and LAI lead to higher deposition velocities over forests compared to other surfaces. For chemicals such as NH_3 that exchange bidirectionally with the atmosphere, gridded values that either ignore bidirectional exchange, or don't consider the potentially compensating contributions of upward and downward fluxes across the heterogeneity of a grid cell can differ from those that do.

Recent studies have begun to examine the impact of downscaling gridded estimates to provide ecosystem-specific values of deposition. Schwede et al. (2018) examined deposition to global forests and contrasted values based on grid-base estimates with land use specific values as predicted by the co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (EMEP) model (Simpson et al., 2012). Their study found differences in deposition up to a factor of 2 between the two values, noting that differences depended on the degree of heterogeneity in the grid cell. Paulot et al. (2018) downscaled deposition values from the NOAA Geophysical Fluid Dynamics Laboratory (GFDL) model to land use specific values. Their results indicate that grid-based results from coarse scale models may underestimate deposition to natural vegetation by up to 30%. Comparison of land-use specific versus grid-average dry deposition fluxes derived from the CMAQ v5.3 with the new Surface Tiled Aerosol and Gaseous Exchange (STAGE, Bash et al., 2018) module further illustrates large differences that can be observed in some locations for HNO_3 and NH_3 (Supplemental Figure S4) even at smaller grid sizes (12 km x 12 km) than the Schwede et al. (2018) and Paulot et al. (2018) studies. The STAGE results are consistent with those studies, as well as Flechard et al. (2011), further emphasizing that the use of gridded deposition values for comparison against ecosystem-specific CLs can be a significant source of uncertainty in the evaluation of exceedances. Ecosystem-specific deposition values are preferred for such assessments.

3.4 Challenges in quantifying uncertainty in total Nr deposition budgets

The previous sections describe numerous sources of uncertainty in deposition estimates derived from CTMs and MMF procedures. Here we use the TDep MMF procedure to illustrate the challenges in developing quantitative estimates of uncertainty in total Nr deposition estimates. The TDep MMF procedure comprises uncertainties associated with:

- measurements of chemical concentrations in air (NH_4^+, NO_3^-, HNO_3) and precipitation (NH_4^+, NO_3^-)

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- spatial interpolation in the fusion procedure
- PRISM estimates of precipitation amount
- CMAQ concentration predictions for unmeasured species
- CMAQ deposition velocities
- incompleteness of the measured and modeled deposition budgets

To estimate total (cumulative) uncertainty in annual total Nr deposition, estimates of uncertainty are first needed at the weekly time scale for individual chemical components of the budget, which then must be propagated to the cumulative uncertainty in weekly total deposition and then to the annual sum of deposition, or weekly uncertainty for individual chemical components must be propagated up to annual and aggregated across chemical components to yield cumulative uncertainty in total annual Nr deposition.

Methods for quantifying some of the sources of uncertainty, such as bias and uncertainty in CASTNET and NADP measurements, are described in previous sections. TDep spatial interpolations employ IDW, for which estimates of uncertainty can be derived using jackknife cross-validation (Willmott and Matsuura, 1995). Note that this only produces an estimate of uncertainty in the interpolation procedure itself, not uncertainty associated with a lack of observations in the interpolation space. The PRISM methodology includes uncertainty estimates for predictions of precipitation amount (Daly, 2008). Lacking measurements of sufficient spatial and temporal representativeness, uncertainty in the CMAQ air concentrations for the non-measured components (Figure 2), as well as deposition velocities, cannot be rigorously evaluated across the CONUS in an operational sense (Dennis et al., 2010).

While it may be possible to derive estimates of some aspects of uncertainty at the weekly time scale of the TDep procedure, methods for aggregating the component uncertainties within and across chemical species and then to the annual scale require development. Furthermore, incompleteness of the measured and modeled budgets with respect to deposition of organic N and other species precludes a quantitative assessment of total uncertainty in the deposition budget.

3.5 Simple metric of uncertainty for total Nr deposition

In the absence of a rigorous estimate of absolute uncertainty, a simpler metric of relative uncertainty, based on current understanding of deposition processes, would be useful to the critical loads community. An example of such an uncertainty metric is developed here using the TDep MMF methodology, though the concept can be applied to ADAGIO as well.

Total deposition at each grid point within the TDep maps comprises HNO_3 dry deposition (HNO_3_dry), particulate NO_3^- dry deposition (NO_3_dry), NH_3 dry deposition (NH_3_dry), particulate NH_4^+ dry deposition (NH_4_dry), dry deposition of non-measured species (NoM_dry, described in Figure 2), wet deposition of NO_3^- (NO_3_wet) and wet deposition of NH_4^+ (NH_4_wet). For the purposes of calculating a metric for uncertainty of a “total” deposition budget, we have added an estimate of wet deposition of unmeasured species (NoM_wet), which is discussed below. Each of these 8 deposition components is first

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assigned a discrete, numerical uncertainty rating from 1 to 5, with 1 representing the lowest uncertainty (most certain) and 5 representing the highest uncertainty (least certain). Uncertainty ratings for individual components do not vary temporally or spatially. Next, for each component of the budget, a weighted uncertainty is calculated as the product of the discrete uncertainty rating (UR_i) for component i of the deposition budget and the fractional contribution of that component to total deposition at the corresponding location ($FTDep_i$). The deposition weighted uncertainty for each component is then summed to estimate the deposition weighted average uncertainty for the total deposition budget, referred to as the weighted deposition uncertainty metric (WDUM).

$$WDUM = \sum (FTDep_i * UR_i) \quad (2)$$

Deposition components and uncertainty ratings are summarized in Table 3. The uncertainty ratings reflect the current level of understanding of deposition processes relative to wet deposition of NH_4^+ and NO_3^-. While there is some uncertainty in the measurements and spatial interpolation of precipitation amount and chemistry and in the PRISM estimates, understanding of the magnitude and spatiotemporal patterns of wet deposition of NH_4^+ and NO_3^- is more complete than for the other components of the TDep Nr budget. Thus, $NH4^+$ and $NO3^-$ wet deposition both have an uncertainty rating of 1 (i.e., lowest uncertainty). The TDep MMF does not include wet deposition of organic N. To incorporate this aspect of uncertainty, we have defined a non-measured wet deposition variable NoM_wet, assumed to reflect the bulk organic fraction of wet N deposition. Based on the global synthesis of wet deposition of organic N reported by Jickells et al. (2013), we assume that NH_4^+ and NO_3^- wet deposition account for 75% of total N wet deposition on average, with NoM_wet accounting for the balance (25%). As it is neither measured or modeled in the TDep procedure, an uncertainty rating of 5 is assigned to NoM_wet, reflecting the highest degree of uncertainty.

Estimates of TDep dry deposition are derived from CMAQ deposition velocities and are therefore inherently more uncertain than TDep wet deposition of $NH_4^+$and NO_3^-. As noted above, HNO_3_dry, NO_3_dry, NH_4_dry are bias corrected using CASTNET measurements. Of the dry deposited species, knowledge of HNO_3 deposition is more complete than for other species. This is reflected in the much higher level of agreement for HNO_3, relative to other N species, between the inferential deposition models summarized in Table 2. HNO_3 dry deposition is primarily governed by atmospheric and boundary layer resistances, as opposed to canopy surface characteristics that are less understood (Wesely, 1989; Zhang et al., 2003). HNO_3_dry is assigned an uncertainty rating of 2, reflecting more uncertainty than wet deposition of NH_4^+ and NO_3^-, but the lowest degree of uncertainty of the dry deposited species.

While modeling of particle dry deposition is advancing, differences among commonly used dry deposition schemes and between models and observations suggest that significant gaps in understanding of the deposition processes remain (Khan and Perlinger, 2017). Understanding of particle dry deposition is generally more limited than that of HNO_3, which is reflected in the greater degree of deviation between dry deposition schemes for NH_4^+ and

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NO_3^- compared to HNO_3 in Table 2. NO_3_dry and NH_4_dry are assigned an uncertainty rating of 3, reflecting a greater degree of uncertainty relative to HNO_3_dry.

TDep NH_3_dry is estimated by CMAQ V5.0.2 using a bidirectional air-surface exchange module (Pleim et al., 2013; Bash et al., 2013), which requires knowledge of the surface characteristics that govern NH3 compensation points as well as surface resistances (Flechard et al., 2013). The process of NH3 air surface exchange is more complex and less understood than HNO_3, as reflected in the greater degree of deviation between NH_3 inferential models in Table 2. Additionally, NH_3_dry is not bias corrected with measured air concentrations. NH_3_dry is subsequently assigned an uncertainty rating of 4. The final component of the TDep dry deposition budget is the non-measured species (NoM_dry) described in section 3.1, which is also estimated using CMAQ. This component of the budget is incomplete with respect to treatment of gas phase and organic N compounds and is not bias corrected. NoM_dry is also assigned an uncertainty rating of 4.

Based on these uncertainty ratings, the WDUM can theoretically range from a value of 1 to 5. An important feature of the WDUM is the implied linear relationship between the uncertainties of the deposition components, which is an obvious oversimplification. For example, the uncertainty for dry deposition of NH_3 may, in reality, be more than a factor of 4 larger than wet deposition of inorganic N. Another oversimplification is the application of a constant uncertainty rating, which ignores spatial and temporal variability. This approach fails to capture, for example, a likely greater level of uncertainty in wet deposition in mountainous terrain (Latysh and Wetherbee, 2012). Additionally, this approach does not reflect uncertainties associated with sub-grid variability in land use previously discussed.

The WDUM for the corresponding 2016 TDep total N deposition map is shown in Figure 4 for the CONUS along with the probability distribution of values. The WDUM ranges from 2.1 to 3.8, with red colors denoting locations with the greatest uncertainty in total deposition. High values of WDUM occur in the Southwest, California Central Valley, and east of the Cascade Mountains in the Northwestern U.S. where the total deposition budget is dominated by dry deposition. High values in eastern North Carolina and some areas of the Midwest reflect a large contribution to from NH_3 dry deposition and corresponding high overall uncertainty. High values in and around urban areas in the Northeast U.S. and cities such as Atlanta, Georgia show areas where NO_2 dry deposition is important. Lowest values occur where wet deposition dominates the budget.

The percent contribution of individual components of the TDep budget to the WDUM for each location is shown in Figure 5. Dry deposition of NH_3 is the largest contributor to uncertainty in the total N budget overall, as reflected in the similarity between NH_3_dry in Figure 5 and the general spatial patterns of WDUM in Figure 4. Uncertainty in dry deposition of non-measured compounds is an important contributor in the eastern U.S., reflecting the importance of NO_2, whereas uncertainty in HNO_3 and NO_3^- dry deposition is important in the Southwest. Uncertainty in dry deposition of NH_4^+ aerosols is a small contributor to the WDUM overall. The wet deposition fraction is dominated by uncertainty associated with organic N dep across the U.S.

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3.6 Using WDUM in assessment of CL exceedances

Knowledge of the level of uncertainty in the total deposition budget can help to inform the level of confidence with which policy and management actions to address CLs can be implemented. Using the distribution of the WDUM to assign ranges of lowest, intermediate, and highest uncertainty is one expression of the WDUM that could be used, akin to the reliability categories for CLs (Bobbink et al., 2003; Pardo et al., 2011). For example, at a near-exceedance site where uncertainty in the deposition estimate is considered low, a land manager may be more confident in implementing an action to achieve the CL.

Using the herbaceous richness CL (Simkin et al., 2016) as an example, Figure 6 illustrates how the WDUM can be used to assess uncertainty at near exceedance sites and its spatial patterns within an area. Combining the information in Figure 6 with the relative contributions of individual components to the WDUM (Figure 5) further allows for the identification of the most important components of the deposition budget with respect to uncertainty. Collectively, this information can be used to develop and prioritize measures to improve deposition budgets and reduce uncertainties for a specific area. This concept is further illustrated below using results for the Croatan and George Washington National Forests and Shenandoah National Park (Table 4).

The Croatan National Forest has 24 (of 60) sites at near-exceedance with an average Nr deposition of 1.1 kg ha^{-1} yr^{-1} (11.5%) below the CL. The average WDUM for the near-exceedance sites is 2.7, reflecting an intermediate level of uncertainty relative to the WDUM distribution (Figure 4). The dominant components of the uncertainty are non-measured wet organic N (NoM_wet, 24.4%) and NH3 dry deposition (23.4%). Enhanced monitoring to refine the deposition budget for this National Forest would prioritize these components.

The George Washington National Forest has 62 (of 431) sites near-exceedance with an average deposition 1.4 kg ha^{-1} yr^{-1} (12.5%) below the CL. Shenandoah National Park has 152 sites (of 327) near-exceedance with an average deposition of 0.5 kg ha^{-1} yr^{-1} (0.1%) below the CL. The WDUM indicates an intermediate level of uncertainty at near-exceedance sites in both areas. Non-measured Nr species again make up the majority of the uncertainty (Shenandoah 37.7%; George Washington 42.9) with NH_3 dry deposition now contributing 34.5% at Shenandoah and 19.6% at George Washington. These two federal land units exist on opposite sides of the Shenandoah Valley. Locations with the highest WDUM values occur on the western slope of Shenandoah and the eastern unit of George Washington. Based on the spatial distribution of the component uncertainties, monitoring and research activities to improve the deposition budgets in these areas would prioritize NO_2 and organic N in George Washington NF and NH_3 in Shenandoah NP.

The near-exceedance sites in the Simkin et al. (2016) dataset all exist in the eastern U.S. Examples of application of the WDUM to CLs for other life forms in the western U.S. are summarized in Table S1. The Bitterroot National Forest (WDUM = 2.9, high) exceeds the CLs for a change in the alpine herbaceous community (3.5 kg ha^{-1} yr^{-1}; Bowman et al., 2012) with the majority of uncertainty coming from dry NH_3 deposition (41.0%). The Columbia River Gorge National Forest (WDUM = 2.9, high) just exceeds the CL for a decrease in lichen richness (3.5 kg ha^{-1} yr^{-1}; Geiser et al. 2019) in an area where lichen play

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an important role in ecosystem stability; dry deposition of non-measured N (34.5%) and NH_3 (20.6%) drive the uncertainty. The Santa Monica Mountains National Recreation Area (WDUM = 3.2, high) exceeds the CL for increased invasive grass growth (11 kg ha^{-1} yr^{-1}; Cox et al 2014) with uncertainty coming from dry non-measured deposition from Los Angeles to the south (30.3%) and dry NH_3 deposition from agricultural emissions from the north (28.6%). Finally, Joshua Tree National Park (WDUM = 2.7, intermediate) exceeds the CL for invasive grass growth which can increase fire risk (2.1 to kg ha^{-1} yr^{-1}; Rao et al. 2010) with the majority of uncertainty coming from dry HNO_3 deposition (31.2%) and dry NH_3 deposition (24.4%). These examples further illustrate how identifying where areas of high uncertainty in deposition overlap with areas of ecological sensitivity can help direct future local efforts to improve deposition budgets for CL assessments.

4 Recommendations

The preceding discussion of sources of uncertainty in Nr deposition budgets motivates research in several areas, including improvements to both measurements and models. Here we outline several key needs for data synthesis, new measurements, and comparisons and improvements to models that will improve the accuracy and spatial representativeness of Nr deposition budgets and facilitate more rigorous estimates of uncertainty.

Deposition budgets used for North American CL assessments are biased low by an unknown yet likely important amount due to lack of measurements of wet and dry organic N deposition and incomplete treatment of organic N in CTMs. An important first step in addressing this bias is to establish standard methods for measuring organic N in precipitation and PM within existing monitoring infrastructure. A goal would be to incorporate routine measurements of bulk organic N into NADP (precipitation), CAPMoN (precipitation and PM) and CASTNET (PM) sampling and analytical protocols. Along with incorporation of organic N measurements in national monitoring networks, a more detailed treatment of organic N in CTMs is also needed (Pye et al., 2015).

Comparisons of measured versus modeled wet deposition of inorganic N across North America generally show biases of ± 30% or less, which is on the same order as the variance among deposition models in the intercomparison studies summarized here. Incorrect spatial allocation and magnitude of emissions and differences in emission inventories are identified as important sources of uncertainty. For NH_3 emissions from animal production in North America, improvements are needed in the emission factors and process-level emission models themselves (McQuilling and Adams, 2015) as well as the accuracy and availability of the activity data (i.e., number and locations of animals, types of) required to develop the inventories (U.S. EPA, 2014). Spatial allocation of emissions will remain an issue until inventories are developed at the animal facility scale but may be better informed by satellite observations. For modeling NH_3 emissions from fertilized soils (Cooter et al., 2012), additional studies are needed to evaluate soil emission potentials (Bash et al., 2013; Zhang et al, 2010) for a wider range of soil types and fertilizer characteristics. Inventories for NH_3 mobile sources also require refinement, as recent measurements indicate emissions from automobiles may be underestimated by a factor of 2 in the U.S. (Sun et al., 2017).

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Improvement of NOx emission inventories are needed to address potential overestimates (~ 30%) in mobile sources (McDonald et al., 2018).

Lack of understanding of dry deposition processes, and subsequent uncertainty in deposition velocities and bi-directional exchange rates, remains a key limitation to improvement of Nr deposition budgets. As noted above, commonly used inferential dry deposition models may differ by a factor of 3 or more in mean deposition (exchange) velocities of Nr species, even when driven with the same inputs (Schwede et al., 2011; Li et al., 2016; Flechard et al., 2011). Additional monitoring and process-level measurements are needed to improve dry deposition models for North America. Establishment of a small number of long-term intensive flux measurement sites (e.g., Harvard Forest, Munger et al., 1996; NitroEurope 'Level 3' sites, Skiba et al., 2009) in key ecosystems is needed to characterize the most important flux processes and to improve their representation in models. Measurements that elucidate non-stomatal and bidirectional (e.g., NH_3) exchange processes and the importance of in- and near-canopy chemistry on canopy-scale fluxes are particularly needed. Low-cost time integrated direct dry deposition methods such as the Conditional Time-Averaged Gradient (COTAG) technique (Famulari et al., 2010) could be deployed in a monitoring mode at a larger number of sites, using existing monitoring infrastructure (e.g., CASTNET), to quantify dry deposition budgets and to provide additional data for evaluation of models.

In addition to new measurements, greater use of existing data would be beneficial. Efforts are underway to develop a database of throughfall measurements across North America to facilitate evaluation of models against independent non-network measurements. A second effort is underway to construct a global metadatabase of micrometeorological flux measurements of Nr (i.e., dry deposition) to help facilitate further evaluation and improvement of dry deposition schemes.

Going beyond the general intercomparisons of CTMs summarized here, more detailed comparisons will be needed to identify the most important sources of uncertainty in wet and dry deposition to prioritize model improvements. For example, the next (fourth) phase of the AQMEII study presents an opportunity to examine the importance of differences in R_c parameterizations for V_d calculations. Other analyses should be performed to assess the importance of meteorology, surface physical characteristics, and atmospheric chemistry to intra-model differences in dry and wet deposition. Mapping this variability between models will yield a more detailed analysis of deposition uncertainty.

In theory, methods such as TDep and ADAGIO that combine measurements and models yield the best possible continuous fields of total Nr deposition currently available. While preliminary comparisons show generally good agreement (75% of observations within ± 30%), more detailed analyses of the magnitude and spatial patterns of agreement, and analysis of the components that differ most, would help to inform a quantitative estimate of uncertainty in total deposition. These should include assessments of the impact of using bidirectional (TDep) versus unidirectional (ADAGIO) models for NH_3 deposition, differences in sources of data for precipitation depth for wet deposition calculations (NADP/PRISM for TDep versus CaPa for ADAGIO), and differences in the fusion method (IDW bias correction for TDep versus optimal interpolation for ADADIO).

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Regarding improvements to MMF procedures, recent studies (Schwede et al., 2018; Paulot et al., 2018) show that the use of grid-average deposition estimates from CTMs can be a large source of error in calculating CL exceedances for some locations. Incorporation of methods such as CMAQ STAGE (Bash et al., 2018) into MMF methods to produce maps of land use specific total deposition should be explored. The TDep MMF procedure does not currently include bias correction for NH_3 due to uncertainty in the IDW parameterization and difficulties introduced by the bi-directional exchange framework. Expanded monitoring to better characterize NH_3 spatial variability in agricultural regions is needed to address these issues. Incorporation of data from existing urban air monitoring networks into the TDep MMF procedure is needed to improve deposition estimates along urban to rural gradients, particularly for NO_2. The use of satellite NH_3 and NO_2 data to inform expanded ground-based monitoring and to fill geographical gaps in monitoring data for MMF applications should be explored.

Incompleteness of deposition budgets with respect to organic N and the complexities of quantifying and aggregating uncertainties in deposition components in CTMs and MMF precludes a rigorous calculation of uncertainty in total Nr deposition. In the absence of a quantitative estimate of absolute uncertainty, we introduce a simpler metric of relative uncertainty in total deposition (WDUM). Our analysis highlights that dry deposition of NH_3 is an important source of uncertainty in many areas of the country. Uncertainty in the dry deposition of oxidized N is important over large areas of the eastern U.S. Examples of uncertainty for specific locations demonstrate the use of the WDUM in identifying the most uncertain components of the budget to prioritize future research and monitoring activities to improve deposition budgets and reduce uncertainties in CL exceedances.

While the metric is presented here in its numerical form, alternative expressions could be considered. For example, delineating ranges of the WDUM as “lowest, “intermediate”, and “highest” levels of uncertainty may be more useful in some decision frameworks or more compatible with approaches such as the reliability rating used for CLs (Bobbink et al., 2003; Pardo et al., 2011). Future work will explore the use of geographical information to incorporate a spatial component to the WDUM to account for greater uncertainty in deposition at higher elevations.

While the WDUM is a useful starting point, an ultimate goal is to generate quantitative maps of total uncertainty that could accompany maps of total deposition such as those developed using TDep and ADAGIO MMF approaches. This will require improvements to measurements and models informed by the recommendations outlined above. Additionally, new methods are needed for aggregating different types of uncertainty estimates within the total deposition budget, including uncertainties derived for measurements, spatial interpolation, bias corrections of air concentrations, probabilistic estimates for modeled variables, and other aspects of MMF procedures. This includes propagation of the uncertainty from the weekly timescale of TDep and ADAGIO to the annual scale.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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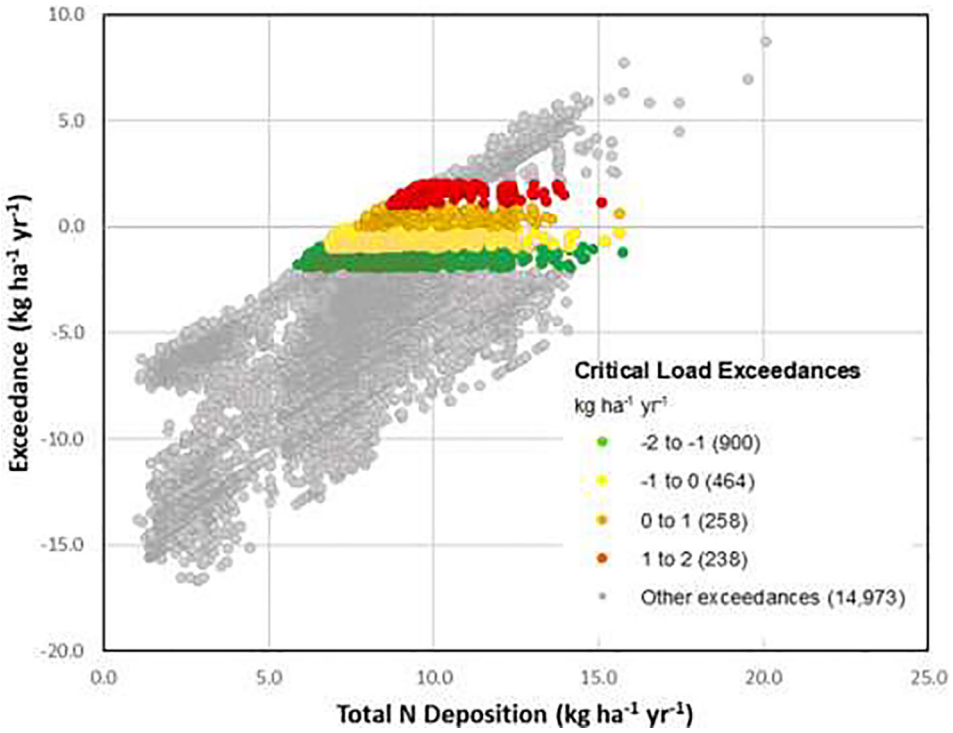

Figure 1.

Exceedance of herbaceous richness critical load based on TDep total N deposition 2013–2015. Colored values represent locations (1860 of 16,833 total) where the exceedance is within ± 2 kg ha^{-1} yr^{-1} of the total N deposition. Exceedance data from Simkin et al., 2016.

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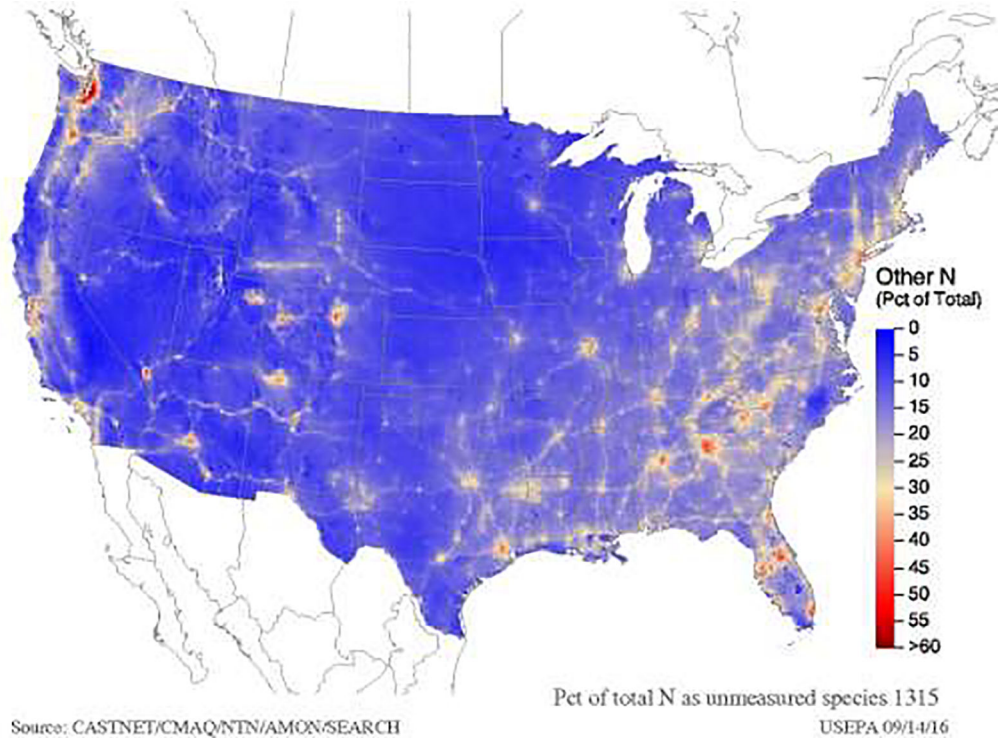

Figure 2.

NADP TDEP map of the percentage of total deposition attributed to dry deposition of non-measured (NoM) N species (i.e. “Other N”), which includes NO, NO_2, HONO, N_2O_5, and organic N.

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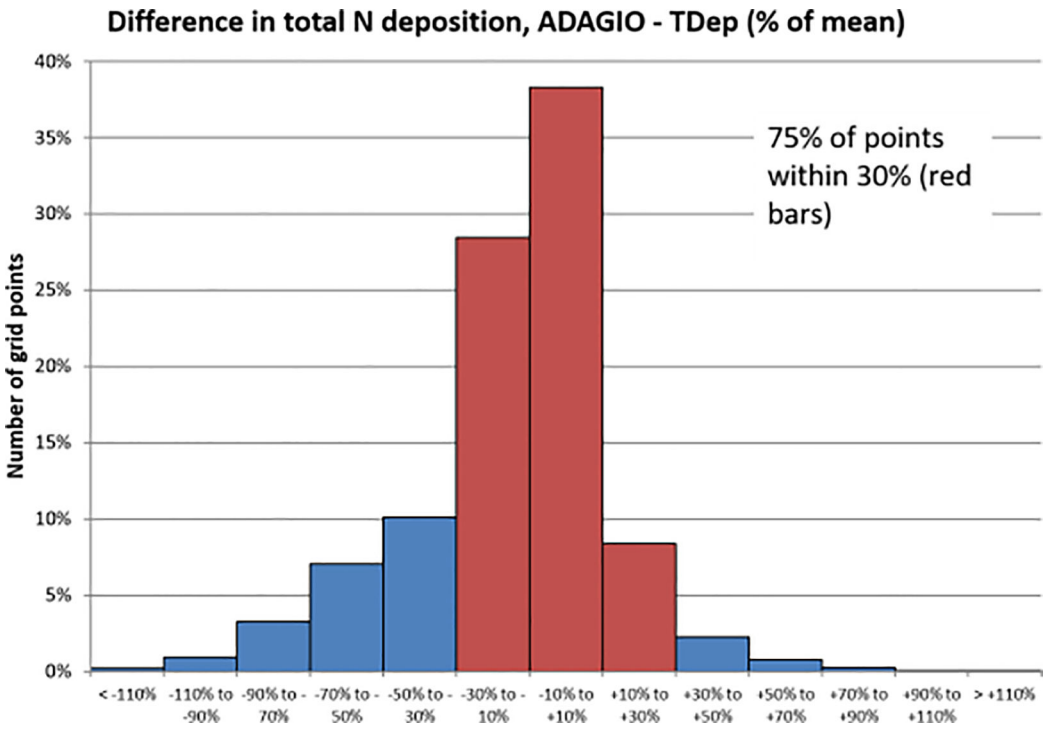

Figure 3.
Comparison of ADAGIO and TDep MMF estimates of total N deposition.

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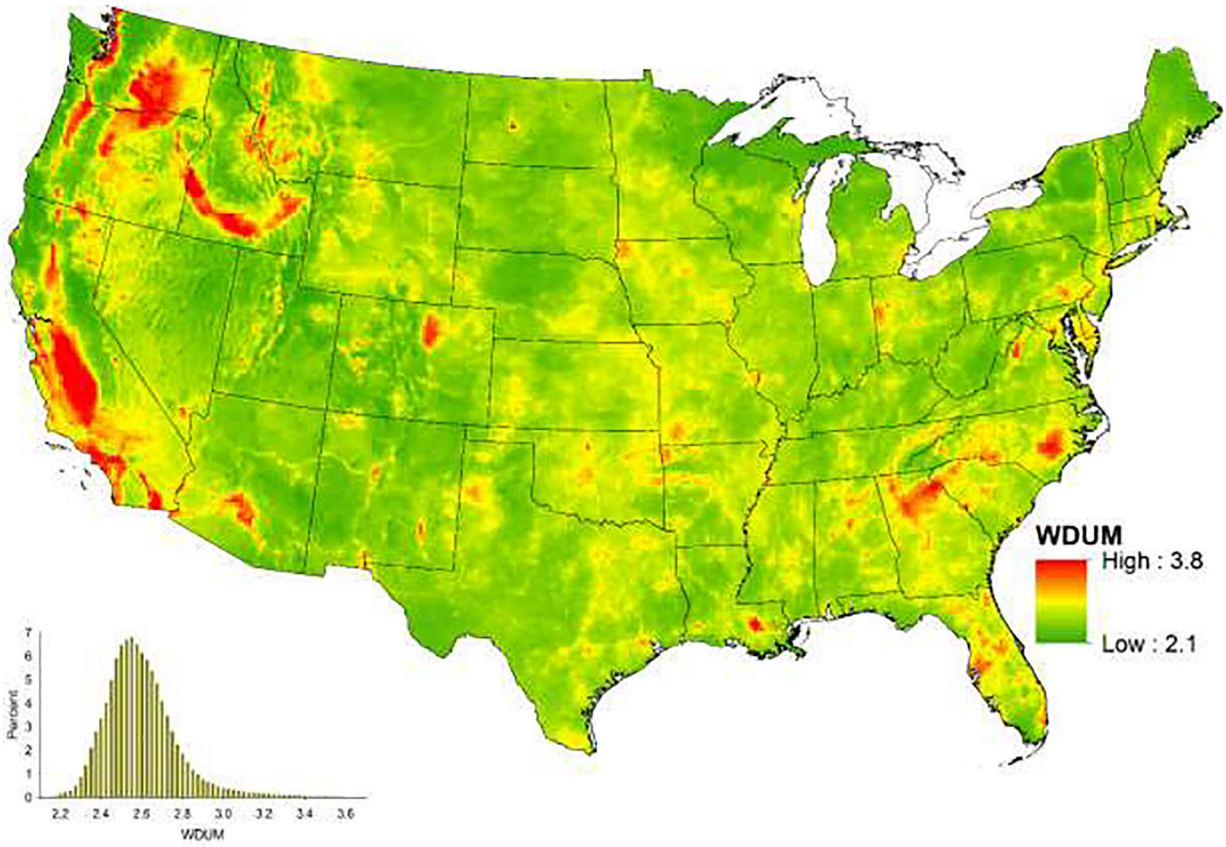

Figure 4.

Map of weighted deposition uncertainty metric (WDUM) for corresponding TDep 2016 total deposition map. Probability distribution of the WDUM (bin-size of 0.025) is inset.

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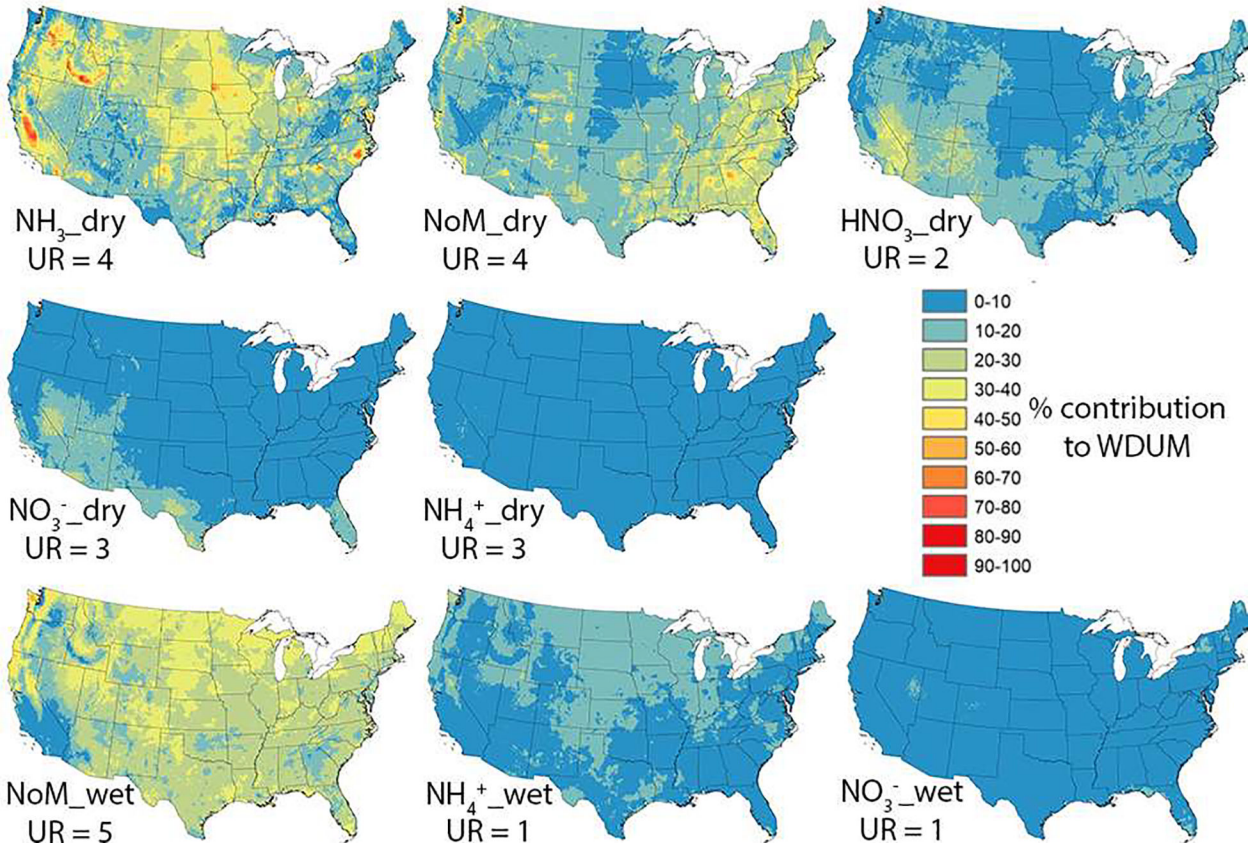

Figure 5.

Percent contribution of components of the TDep total N deposition budget to the corresponding WDUM values shown in Figure 4. Uncertainty ratings (UR) used in equation (2) and described in Table 3 are also indicated.

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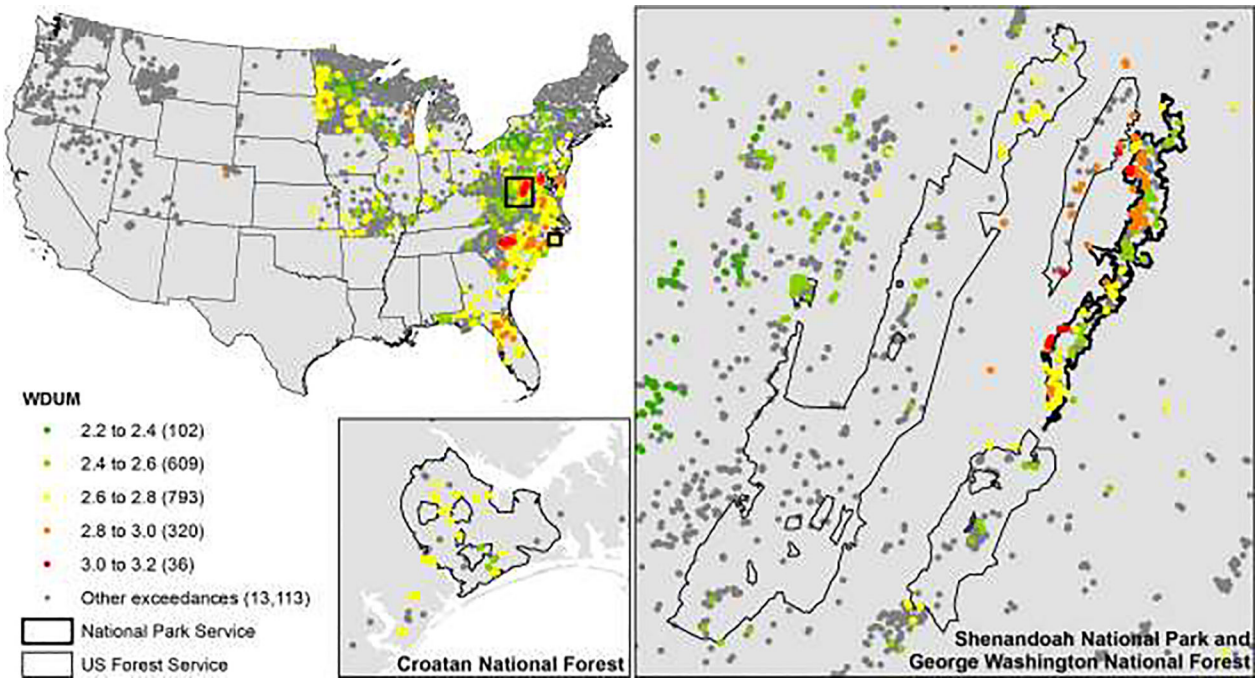

Figure 6.

WDUM for near exceedances (± 2 kg ha^{-1} yr^{-1}) of the herbaceous richness critical load based on TDep total N deposition 2013–2015. Inset maps show distribution of survey plots from Simkin et al., 2016 within Croatan National Forest, George Washington National Forest, and Shenandoah National Park.

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Table 1.

Evaluation of multi-model mean wet deposition valúes with NADP measurement data. For all parameters, the ideal value is 1.0.

			NO_3^- wet dep			$NH4^+$ wet dep		
Project	**Model year**	**Data years (averaged)**	**Linear fit slope**	**Correlation coefficient**	**Fraction within 50%**	**Linear fit slope**	**Correlation coefficient**	**Fraction within 50%**
PhotoComp	2000	2000–2002	1.0	0.8	0.77	0.8	0.9	0.82
ACCMIP	2000	2000–2002	0.9	0.9	0.69	0.5	0.8	0.76
HTAP I	2000	2000–2002	1.0	0.9	0.84	0.9	0.9	0.85
HTAP II	2010	2009–2011	1.2	0.9	0.67	0.8	0.9	0.88

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Table 2.

Statistical results of the relative standard deviation (%) of annual dry deposition fluxes produced by four inferential models applied at sites within the NitroEurope network[a]. Summarized from Flechard et al. (2011).

Site type	N	NH_3 - N				HNO_3 - N				NO_2 - N				NH_4^+ - N				NO_3^- - N				Total N			
		Mean	Med	Min	Max	Mean	Med	Min	Max	Mean	Med	Min	Max	Mean	Med	Min	Max	Mean	Med	Min	Max	Mean	Med	Min	Max
F	29	50	49	35	75	28	27	19	46	76	73	58	100	86	85	67	107	78	74	63	115	43	44	26	59
SN	9	50	49	44	67	10	12	0	18	79	81	67	85	48	43	20	84	50	38	29	128	37	35	29	49
G	8	190	81	51	872	7	7	0	16	69	77	38	86	36	34	22	77	38	38	18	55	67	52	38	157
C	8	137	109	48	367	11	12	0	15	75	76	67	85	64	56	49	118	62	59	46	99	63	54	44	124
ALL	54	83	51	35	872	20	20	0	46	76	76	38	100	69	76	20	118	65	67	18	128	49	44	26	157

[a]Note: The four models are the UK CBED scheme, the Dutch IDEM model, the dry deposition module of the Environment Canada model, and the surface exchange scheme of the EMEP model used under the CLRTAP. For details see Flechard et al. (2011). N: number of sites at which the models were compared, F: forest, SN: semi-natural short vegetation, G: grassland, C: cropland. The relative standard deviation (RSD) for each N species and for each site is calculated as SD/Mean × 100%, where SD and Mean are the standard deviation and mean value of the annual fluxes produced by the four models. Statistics of the RSD are then calculated and reported in the table above for each site type and for all sites (ALL) where Mean is the mean value of the RSD, Med: median value, Min: minimum value, and Max: maximum value.

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Table 3.

Summary of deposition components and uncertainty ratings for the weighted deposition uncertainty metric (WDUM).

Deposition Component	Description	Uncertainty Rating
NO_3_wet	Wet deposition of NO_3^-	1
NH_4_wet	Wet deposition of NH_4^+	1
NoM_wet	Wet deposition of ON (non-measured)	5
NO_3_dry	Dry deposition of NO_3^-	3
HNO_3_dry	Dry deposition of HNO_3	2
NH_4_dry	Dry deposition of NH_4^+	3
NH_3_dry	Dry deposition of NH_3	4
NoM dry	Dry deposition of “other N” species	4

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Table 4.

Summary of total deposition (TDep, Total N 2013–2015), exceedances (Exceed), WDUM, and percent contribution of deposition components to WDUM (% of WDUM) for Simkin et al. (2016) points (Count) that fall within the boundaries of the Croatan and George Washington National Forests, and Shenandoah National Park.

	Croatan NF		George Washington NF		Shenandoah NP	
	All	**Near Exceedance**	**All**	**Near Exceedance**	**All**	**Near Exceedance**
Count	60	24	431	62	327	152
TDep	8.5	8.6	7.6	8.4	9.7	10.3
Exceed	−2.9	−1.1	−3.9	−1.2	−2.0	−0.5
WDUM	2.7	2.7	2.5	2.6	2.7	2.8
		% of WDUM		*% of WDUM*		*% of WDUM*
HNO_3_dry	5.8	5.8	17.5	18.1	13.4	12.3
NH_3_dry	**22.9**	**23.4**	15.1	19.6	**29.4**	**34.5**
NH_4_dry	2.6	2.6	2.6	2.9	1.9	1.7
NH_4_wet	9.6	9.3	8.2	7.5	7.9	7.2
NO_3_dry	10.8	11.0	3.0	3.3	2.2	2.0
NO_3_wet	5.4	5.4	6.5	5.7	4.9	4.6
NoM_dry	17.8	18.1	**22.6**	**20.9**	19.1	17.9
NoM_wet	**25.0**	**24.4**	**24.4**	**22.0**	**21.3**	19.8