Earth's Future

Greater Contribution From Agricultural Sources to Future Reactive Nitrogen Deposition in the United States

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Abstract Many sensitive ecosystems in areas protected for biodiversity conservation in the United States suffer from exposure to excess reactive nitrogen (Nr) released by fossil fuel combustion and agricultural practices and deposited onto the land surface and water bodies. The Community Multiscale Air Quality (CMAQ) model was applied over the contiguous United States to link emissions and climate change to reactive nitrogen deposition by simulating both present-day and future speciated Nr deposition to protected areas. Future conditions included examining the Representative Concentration Pathway 8.5 climate and the Shared Socio-Economic Pathway 5 emission scenarios. We further identify protected areas that would benefit most from better Nr management strategies by comparing the simulated deposition with multiple critical loads (CLs) for both biodiversity and acidification in terrestrial and aquatic ecosystems. Achieved by further NO$_x$ emission reductions from the mobile and power generation sectors, future Nr deposition is expected to decrease. However, in regions with intensive fertilizer application or hosting concentrated animal feeding operations, the reduction may be offset by rising agricultural NH$_3$ emissions. The protected areas having CL exceedances in 2050 are expected to increase by 5.5% for empirical lichen-based CL, and by 11% and 22% for surface water and forest soil acidity, respectively, because of the agricultural NH$_3$ emission increase. By linking the deposition simulations with a water quality model, we identified that atmospheric deposition is the dominant source of nitrogen for several remote watersheds, including several lakes in National Parks and National Wilderness areas in Colorado, Montana, and Minnesota.

1. Introduction

As one of the major elements for building proteins and DNA, nitrogen in reactive forms (Nr) is critical to all life. However, excessive release of Nr from human activities (e.g., food production and fossil fuel combustion) is now exerting adverse impacts on human and ecosystem health in many regions worldwide (Galloway et al., 2008, 2014; Stevens, 2019). The enormous amount of anthropogenic Nr input in intensified agriculture areas is believed to be far exceeded for a sustainable nitrogen cycle (Battye et al., 2017; Steffen et al., 2015). As it cascades through the environment, the same atom of nitrogen emitted into the atmosphere transforms into a sequence of different forms and causes multiple effects in series, including air quality degradation (via ozone and aerosol formation) and deposition leading to alterations in natural ecosystems productivity, acidification of soils and surface waters, eutrophication in freshwaters and coastal marine ecosystems, biodiversity loss, and production of N$_2$O (an important greenhouse gas) (Galloway et al., 2003).

During the past two decades, Nr deposition in the United States has shifted from an oxidized Nr-dominated (Nr-ox) pattern to a reduced-Nr-dominated (Nr-red) pattern because nitrate (NO$_3^-$) deposition has been decreasing due to successful emission controls of NO$_x$ from mobile sources, energy generation units, and other sources (Dallmann & Harley, 2010; Kim et al., 2006; Li et al., 2016). Further reduction of Nr emissions from fossil fuel combustion is expected to continue in the near future with more stringent air quality and emission standards, as well as the shift to natural gas (Campbell et al., 2018; Paltsev et al., 2011). In contrast, ammonia (NH$_3$) emission from agricultural sources continues to rise, exacerbated by the growth of both

domestic and export food demand (Galloway et al., 2007; National Research Council (NRC), 2008). For crop production, the amount of surplus nitrogen remains high over the past decades despite an improved nitrogen use efficiency (NUE) because a rising amount of fertilizer is applied, resulting in Nr-red loss to the environment (Zhang et al., 2015). Increased meat consumption also raises Nr emission and discharge from animal manure handling (Zeng et al., 2019). Greater contribution from agriculture sources to the environment Nr load is expected in the foreseen future, as more food is needed to sustain a growing population. The rising temperature under climate warming will also favor the release of NH_3 from vegetation, soil surface, and farms (Bash et al., 2013; Massad et al., 2010; Shen et al., 2020; Sutton et al., 2013). Agricultural sources will contribute to Nr deposition to a larger extent if more energy needs will be met by biofuel (Davis et al., 2016). As a result, the decrease in Nr deposition achieved by controls on mobile sources and power generation may be canceled out by increasing Nr release from agricultural sources. How future changes in emission sources and climates will affect Nr deposition has only been sparsely investigated (Church & Van Sickle, 1999; Ellis et al., 2013; Tagaris et al., 2008).

Although atmospheric deposition is a relatively minor nitrogen source to streams in urban and agricultural catchments, it is usually the dominant source of Nr in remote areas such as headwater lakes and sensitive streams (Baron et al., 2011; Ellis et al., 2013). Knowing which watersheds may be more vulnerable to Nr deposition increase when agricultural emissions rise in the future can help identify the regions that will benefit more from agricultural Nr management.

Critical loads (CLs) provide quantitative estimates of the thresholds below which the exposure to a pollutant is not expected to cause a significant adverse effect over the long term based on the current knowledge (Nilsson & Grennfelt, 1988). To understand the ecological impacts of Nr deposition, the deposition amounts are compared with the CLs and exceedances for CLs indicate the likelihood of an ecosystem suffering from excess nitrogen deposition under current and future scenarios (Ellis et al., 2013). It should be noted that a given location can have multiple CL values depending on the receptors and/or the biogeochemical process of concern. The CL values also vary by estimation approach, including empirical, steady-state and the dynamic modeling approaches (USEPA, 2008a). There is a growing number of studies assessing the CL of nitrogen for the nutrient enrichment or acidification effects in surface water bodies and terrestrial ecosystems both at national and regional scales (McNulty et al., 2007; Pardo, Fenn, et al., 2011; Scheffe et al., 2014). A national CLs database for nitrogen and sulfur was developed by the National Atmospheric Deposition Program to gather published CLs data for the United States (Lynch et al., 2017). CLs for different receptors and targeted ecological responses can vary by orders of magnitudes (Lynch et al., 2017). Hence, it is important to evaluate the Nr deposition against multiple CLs to better inform future Nr management to protect and maintain various functions and services of ecosystems.

Here, by incorporating population- and climate-driven Nr emission changes from agricultural sources and policy regulated Nr emission changes from fossil fuel combustion sources, we simulate historic (2010) and future (2030 and 2050) atmospheric Nr deposition over the contiguous United States (CONUS) under the Representative Concentration Pathway (RCP) 8.5 ($RCP_{8.5}$) scenario (a climate scenario generally representative of an intensely warming future). In addition, we link a water quality model with an atmospheric chemical transport model to estimate the impact of Nr deposition change on total Nr loading over the CONUS in 61,117 watersheds (median size = 60 km^2) at the scale of 1:500,000. The impacts of simulated Nr deposition is also examined in the context of CL datasets targeted for multiple ecological endpoints (e.g., surface water acidity, forest soil acidity, and biodiversity) to identify regions that were predicted to be adversely affected by Nr deposition. We further analyze the contribution of emission changes from agricultural sources to Nr deposition, mainly focusing on the identified vulnerable regions. Results of this study provide insights into spatially resolved priorities to mitigate adverse impacts of Nr deposition by controlling Nr sources.

2. Materials and Methods

2.1. Modeling and Evaluating Nr Deposition

The Community Multiscale Air Quality Modeling System (CMAQ) is a regional air quality model that has been widely applied to simulate the concentration and deposition of atmospheric pollutants (Appel et al., 2011, 2012; Byun & Schere, 2006). In this study, CMAQ v5.0.2 is used to simulate Nr deposition (USEPA, 2014a). A total of 14 Nr species are considered in the model, including nitric oxide (NO),

nitrogen dioxide (NO_2), nitrate radical (NO_3), dinitrogen pentoxide (N_2O_5), nitric acid (HNO_3), nitrous acid (HNO_2), peroxy-nitric acid (HNO_4), organic nitrate (RNO_3), peroxyacetyl nitrate (PANs), and NH_3, as well as ammonium (NH_4^+) and nitrate (NO_3^-) aerosol. The study domain covers the CONUS with a horizontal resolution of 36 km by 36 km and vertical layers extending up to ~16 km. The specific model configurations including chemical mechanism and physical processes schemes are presented in Appel et al. (2011). Particularly, we focus on the Nr deposition to protected areas for biodiversity conservation defined by U.S. Geological Survey (USGS) (referred to as protected areas hear after). The extent of protected areas in each simulated grid cell is derived from a GIS layer at 1 km by 1 km resolution (USGS, 2018).

The meteorological fields in 2010, 2030, and 2050 are downscaled using the Weather Research and Forecasting (WRF) model Version 3.8.1 (Bruyère et al., 2014) from the bias-corrected climate projections under the $RCP_{8.5}$ (IPCC, 2014). $RCP_{8.5}$ is a climate scenario representative of an intensely warming future. The climate projections data are obtained from Ensemble Member #6, generated from the National Center for Atmospheric Research's Community Earth System Model version 1 (CESM1) (Monaghan et al., 2014). Spectral nudging is applied to temperature, geopotential heights, and horizontal winds. The downscaled meteorological fields showed average warming of 1.67°C and reduced precipitation of 6.4 mm between 2010 and 2050 over the CONUS with great spatial variation (Figure S1 in the supporting information). The detailed downscaling techniques have been described in a previous study (Shen et al., 2019).

The emissions in 2010 are generated from the EPA 2011 air emissions modeling platform v6.1 based on the 2011 National Emissions Inventory (NEI) (USEPA, 2014b). Emissions in 2030 and 2050 are projected by sector. Two previous studies have projected emissions from agricultural sources based upon their response to climate factors and population growth. NH_3 emissions from fertilizer applications are obtained from Shen et al. (2019), which estimated the change of emission-related processes and agricultural practices in response to climate change using a coupled agroecosystem-air quality model (i.e., FEST-CMAQ with NH_3 bidirectional exchange model) (Yang et al., 2017). The projection of livestock waste management emissions follows a previous study that used a regression model based on the growing population and demands for different animal groups to project future emission trends (Chen et al., 2019) (Figure S2). Emission projections for both fertilizer application and livestock waste management assume the mitigation measures to improve NUE and abatement approaches to reduce atmospheric NH_3 emissions remain unchanged at present-day level. For other anthropogenic sources, the 2011 NEI emissions are used as the starting point, whereby sectoral-specific growth factors are applied based on the Shared Socio-Economic Pathway 5 (SSP5) (Kriegler et al., 2017) for projecting emissions. SSP5 represents a scenario featuring high fossil fuel consumption and food demand, which will result in a radiative forcing pathway close to the $RCP_{8.5}$. Biogenic emissions are obtained from Shen et al. (2019), which simulated present-day and future biogenic emissions with the Biogenic Emission Inventory System (Pierce et al., 2002) (Figure S3). Future Nr emissions from fires are adjusted based on the 2011 NEI emission data and the gridded future-to-current ratios of fire-induced column nitrogen loss predicted by CESM1 (NCAR, 2011). Hereafter, we will refer to the future scenario with projections for all sources as "Ag_projected." In addition, we simulate a contrasting future scenario where all other sources are projected but the NH_3 emissions from agricultural sources remain unchanged after 2010 (Ag_fixed). The influence of agricultural NO_x emission is not included because it cannot be easily isolated from biogenic emissions from other land types in BEIS. Although the impact of agricultural NO_x emission can be high in agriculturally intensive areas (Almaraz et al., 2018), the contribution is expected to be minor on the national scale.

To evaluate the model performance, the modeled concentration of Nr species are compared with the measured concentrations obtained from the Clean Air Status and Trends Network (CASTENET) (USEPA, 2019a) (Figure S4). The modeled NH_4^+ and NO_3^- depositions are compared with wet deposition measurements obtained from the National Atmospheric Deposition Program-National Trends Network (NADP-NTN) (NADP, 2019) and dry deposition estimates from CASTENET (USEPA, 2019a) (Figure S5). The modeled total depositions (dry and wet) are also compared with the sum of dry deposition estimates from CASTNET and wet deposition measurements from NADP-NTN at collocated sites (Figure S6). Meteorological fields derived from the North American Regional Reanalysis database (NOAA, 2019) are used to drive the CMAQ simulations for evaluating model performance purpose. The CMAQ simulated concentrations agree well with the observations (Figure S4), except for NO_3^-, which deviates from the observed

concentrations when the relative humidity is below 60%. To eliminate the bias introduced by modeled precipitation, the measured precipitation is used to adjust the modeled wet deposition fields (Appel et al., 2011). Overall, CMAQ captures the spatial distribution of annual NH_4^+ and NO_3^- deposition in both dry and wet forms with a normalized mean bias ranging between 0.1 and −0.5 (Figure S5), except for NO_3^- dry deposition. Prior studies suggest that the NO_3^- deposition may be biased due to overestimated dry deposition velocity for NO_3^- (Shimadera et al., 2014). Besides, the dry deposition estimates from CASTNET based on atmospheric concentrations and modeled deposition velocities are usually found to be biased low because (1) the weekly integrate sampling protocol of atmospheric concentrations misses daily and diurnal variations (Fenn et al., 2009); (2) the modeled deposition velocities can be very inaccurate when influences from local meteorological condition, and terrain and canopy characteristics are complex (Weathers, 2011); and (3) NO_3^- and HNO_3 partitioning is biased due to the volatility of NH_4NO_3 particles on filters (Walker et al., 2019). There is a lack of routine measures to evaluate the modeled dry deposition of $NH_3(g)$, but the modeled and observed NH_3 concentrations agree well (Figure S4). In general, although the modeled total NO_3^- and NH_4^+ deposition agrees well with the dry and wet deposition sum from CASTNET and NADP-NTN collocated sites, more reliable measurements covering a wide range of landscapes and Nr species are needed to fully evaluate and constrain the uncertainties in the model-predicted Nr deposition amount (Walker et al., 2019).

In addition to Nr species, we also investigate other compounds that are associated with Nr deposition. Sulfate concentrations are expected to further decrease because of further emission controls of energy generation units, and this will modify Nr deposition because the abundance of sulfate will influence the gas and particle partitioning of ammonia/ammonium and nitric acid/nitrate (Paulot et al., 2013). We calculate the normalized brute-force sensitivity of total Nr deposition to sulfate concentration in each grid cell based on the SO_2 sensitivity scenarios developed by a previous study (Chen et al., 2019). The sensitivity is calculated using the equation below,

$$S_{Nr, SO_4^{2-}} = \frac{\left(Nr_{dep,\ baseline} - Nr_{dep,\ perturbation}\right)/Nr_{dep,\ baseline}}{\left(\left[SO_4^{2-}\right]_{baseline} - \left[SO_4^{2-}\right]_{perturbation}\right)/\left[SO_4^{2-}\right]_{baseline,}}$$

where $Nr_{dep,baseline}$ and $Nr_{dep,perturbation}$ represent the total Nr deposition amount in the baseline scenario and a sensitivity scenario in which SO_2 emissions are further reduced by 75%, respectively. $(SO_4^{2-})_{baseline}$ and $(SO_4^{2-})_{perturbation}$ represent the ambient sulfate concentration in the corresponding scenarios, respectively.

2.2. CLs

To identify the areas requiring further Nr deposition reduction, we compare the amount of simulated Nr deposition with CLs associated with different biogeochemical and ecological endpoints including surface water acidity, forest soil acidity, and biodiversity in terrestrial ecosystems. The CL data are obtained from the National CLs Database (NCLD) for nitrogen and sulfur developed by the National Atmospheric Deposition Program (Lynch et al., 2017). CL data for surface water and forest soil acidity are mapped onto the 36 km by 36 km CMAQ grid employed here. The average and 10th percentile values are used for comparison, representing moderate and protective criteria, respectively (Figure S7). The CL values for forest soil and aquatic acidity are combined for sulfur and nitrogen deposition, defined as a three-node linear CL function (Lynch et al., 2017). The CL for forest soil acidity is derived using a steady-state mass balance model (McNulty et al., 2007). The CL for freshwater acidity is derived using a steady-state water chemistry model (Scheffe et al., 2014). Major processes affecting base cations, anions, and nitrogen loading as well as the acid neutralization capacity (ANC) were considered in simulating the CLs. It should be noted that although the variation in CLs among different sites within each grid cell is considered in this study, the uncertainty associated with CL estimates for each site is not incorporated. Both CL model estimates for forest soil and surface water acidification are subjected to high uncertainties in key model parameters such as soil base cation weathering rate and ANC (Li & McNulty, 2007; Scheffe et al., 2014). The lichen-based CL was selected to represent the empirical CL for nitrogen for terrestrial ecosystems because the shift in dominant lichen species is a sensitive bioindicator of Nr level and community diversity loss in terrestrial ecosystems (Pardo,

Robin-Abbott, et al., 2011). The lower end of the empirical CL range reported for each ecoregion is adopted for CL exceedance assessment to provide a more conservative estimation. Steady-state CL and empirical CL values provide estimates of the deposition levels allowable to maintain ecosystem sustainability over the long term. Comparison between the deposition levels and CLs in this study thus provide insights into whether Nr deposition exceeds thresholds in the present-day or future scenarios, however, without considering the dynamic response of the ecosystem to changing Nr deposition.

2.3. Water Quality Modeling and Total Nr Loads

We link the CMAQ deposition fields with the USGS water quality model, SPARROW (SPAtially Referenced Regressions On Watershed), (Schwarz et al., 2006) to qualitatively estimate the main source of total Nr load for each of 61,117 watersheds over the CONUS. We also use the SPARROW model to simulate the mean annual flux of total Nr load in streams as a function of 10 nutrient sources, six climatic and landscape factors that influence nutrient delivery to streams, and nutrient removal in streams and reservoirs. Nutrient sources include atmospheric deposition of nitrogen, urban and population-related sources (i.e., industrial and municipal wastewater treatment plants, septic systems, and urban runoff), and eight sources in the runoff and subsurface flow based on the underlying surface, including forest, shrub, barren land, and animal farms and four types of cropland (corn and soybean, alfalfa, wheat, and other crops) (Alexander et al., 2008). The SPARROW model calibration is based on the long-term mean annual load of total nitrogen at stream monitoring sites across the CONUS, following Alexander et al. (2008). Overall, the modeled total nitrogen flux has an R^2 of 0.933 and root-mean-square error of 0.553 on log scale, which translates to a 95% confidence level of approximately a factor of two for flux predictions for individual stream reaches (Alexander et al., 2008). To quantify the impact of the change in atmospheric Nr deposition on total Nr loading in streams, we performed three SPARROW simulations using CMAQ-simulated Nr deposition fields from the "present-day," "Ag_projected," and "Ag_fixed" scenarios. Other variables, including urban population and agricultural land areas, and the corresponding source strengths remain unchanged at present-day level (USEPA, 2019b; Wimalasekera, 2015). The difference between the SPARROW simulations in "present-day" and "Ag_projected" scenarios characterizes the change in total Nr loading driven by the change in total deposition between 2010 and 2050. The difference between the SPARROW simulations in "Ag_projected" and "Ag_fixed" scenarios characterizes the change in total Nr loading driven by the change in deposition due to rising agricultural NH_3 emissions. The uncertainty in the predicted change in total Nr load mainly depends on the uncertainty of source coefficients for atmospheric nitrogen deposition (standard error = 14.4%), which is smaller than the overall model uncertainties.

3. Results and Discussion

3.1. Nr Emissions Changes Between the Present-Day and Future Scenarios

We examine the changes in NH_3 emissions from agricultural sources, together with Nr emissions from other sources (i.e., NO_x emission from biogenic sources, NH_3, NO_x, and particulate NH_4^+ and NO_3^- emissions from agricultural waste burning, wildfire, mobile sources, energy generation, and other unspecified point and area sources) between 2010, 2030, and 2050. Emission trends follow the SSP5 socioeconomic pathway under the $RCP_{8.5}$ climate scenario. Agricultural emissions under $RCP_{8.5}$ represent a higher end of the emissions projected across RCP scenarios (Shen et al., 2020). In addition, the projections of agricultural NH_3 emissions do not include further adaptation to improve NUE in crop and livestock production under the changing climate. Adaptive measures such as replacement of urea with nonurea fertilizers, deep placement of fertilizers, optimizing feeding plans for animals are expected to lower the NH_3 emission in the future even under warmer conditions and higher food demand (Kohn, 2015; Shen et al., 2020). On the other hand, SSP5 generally exhibits a rapid decline in pollutant emissions from other anthropogenic sources due to pollution controls (Rao et al., 2017). In total, Nr emissions in the United States are projected to decrease by 27%, from 7.7 Mt-N yr^{-1} in 2010 to 5.6 Mt-N yr^{-1} in 2030, and climb up back to 6.4 Mt-N yr^{-1} in 2050 in this specific case (i.e., $RCP_{8.5}$ + SSP5) (Figure 1a). The emissions of Nr-ox (mainly as NO) will decrease from 4.4 Mt-N yr^{-1} in 2010 to 2.1 Mt-N yr^{-1} in 2030. The emission rate in 2050 (2.6 Mt-N yr^{-1}) is higher than that in 2030 mainly because of the increase of NO_x from biogenic sources and fires caused by warming, part of which originated from the cropland emissions. In contrast, the total emission of Nr-red (mainly as NH_3) climbs up steadily from 3.2 Mt-N in 2010 to 3.8 Mt-N in 2050 because of emissions increases in
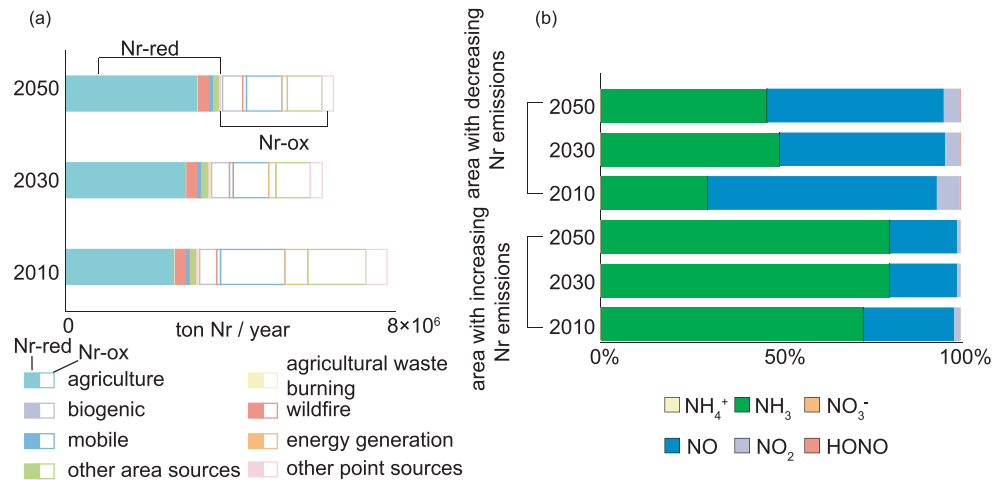
Figure 1. Sectoral Nr emissions changes between the present-day (2010) and future (2030 and 2050) scenarios. (a) The change in absolute amount of Nr emissions and the breakdown of oxidized and reduced forms of Nr from agricultural sources and other sources. (b) The change in Nr emission profiles for areas with increasing and decreasing Nr emissions, respectively. NH_3 emissions from agricultural sources are zero because they are aggregated as biogenic NO_x emissions in Biogenic Emission Inventory System (BEIS) model simulations.

agricultural sources associated with growing food demand and warming. Besides, the NH_3 emissions from mobile and other fossil fuel combustion sources only decrease by ~3% between 2010 and 2050 while NO_x emissions from these sources are significantly reduced, resulting in an increase in the relative contribution of NH_3 emissions to total Nr emissions. The trend has already been identified in urban regions of CONUS (Sun et al., 2017). As a result, the emissions of Nr-red outweigh that of Nr-ox in 2050. Similar trends have been reported in previous studies (Lamarque et al., 2011; van Vuuren et al., 2011).

Spatially, Nr-red emissions from agricultural sources will make a major contribution to total Nr emissions in more widespread areas in the future in central and southeastern United States, as well as California, while Nr emission reduction is expected to occur in populous metropolitan areas dominated by combustion sources. Sixty-three percent of the land area over the CONUS will see increases in Nr emissions due to the emission increase from agricultural sources (Figure S8). For these areas, NH_3 emissions account for 58% of the total emission of Nr. Even in areas with decreasing Nr emissions, the contribution from NH_3 will also increase from 32% in 2010 to 46% in 2050 (Figure 1). As a result, most areas will switch from Nr-ox-dominated in 2010 to Nr-red-dominated in 2050 (Figure S9), and the percentage of areas dominated by agricultural Nr emissions will increase from 49% in 2010 to 67% in 2050.

3.2. Nr Deposition Changes Between the Present-Day and Future Scenarios

Nr deposition is simulated for 2010, 2030, and 2050 with a focus on protected areas. Generally, total Nr deposition over the protected areas declines during the projection period (Figure 2). From 2010 to 2030, the deposition amount shows a decrease of 23% mainly driven by a significant decrease in oxidized-Nr deposition (by 41% between 2010 and 2030). The decrease in Nr-red driven by other factors including emission changes from fossil fuel combustion sources is much smaller than the decrease in Nr-ox partly because NH_3 is being emitted as a byproduct for NO_x emission control when NO is over reduced, which may contribute as a major source to Nr deposition in urban regions (Bettez & Groffman, 2013; Fenn et al., 2018). However, the trend of the total Nr deposition becomes flat beyond 2030 when the decrease in oxidized-Nr deposition slows down and is offset by a steady increase in the reduced-Nr deposition. As a result, the increase in the Nr deposition is mostly in the reduced form consistent with the shift in compound profiles of the future Nr emissions (Figure S9). The temporal trend for the CONUS is similar to that for the protected areas, although the magnitude of change is slightly smaller (Figure S10). The increasing trend in reduced-Nr deposition and the decreasing trend in total Nr deposition are accordant with the observed historical trends, which have shown an increase in NH_3 deposition since the 1980s and a decrease in total inorganic nitrogen deposition since the late 1990s (Du, 2016; Li et al., 2016). Our projection of a specific scenario indicates that
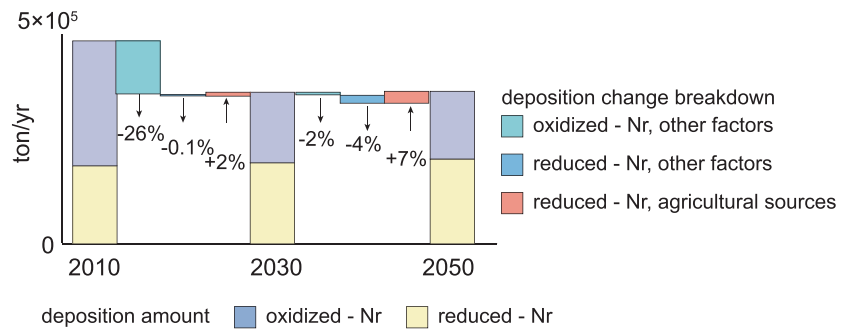
Figure 2. Projected changes in total deposition of Nr in protected areas over the CONUS from 2010 to 2050 in the "Ag_projected" scenario (stacked bars). The changes attributed to agricultural sources and other factors including emission changes in other sources and meteorological conditions are also displayed.

the decreasing historical trend in total Nr deposition could be reversed by the increase in reduced-Nr deposition due to growing agricultural emissions.

Due to further NO_x emission control in the future, the total Nr deposition is expected to decrease in most (91%) of the CONUS in 2050. For the rest of the areas, the estimated rise in total Nr deposition is driven by enhanced agricultural NH_3 emissions. Spatially, areas associated with concentrated animal feeding operations (CAFOs), especially for hogs and poultry, are hot spots showing the highest increases in Nr deposition during the projection period (Figure 3). These hot spots are concentrated in a few states, including Iowa, North Carolina, Georgia, and Arkansas (Figure 3). Large-scale increases in Nr deposition are found in the northern part of the central United States because of the warming-induced increase in ammonia volatilization over cropland which outweighs the decrease in NO_x emissions. Across the CONUS, the proportion of land surface receiving more Nr-red than Nr-ox will increase from 37% in 2010 to 83% in 2050 (Figure S11), emphasizing the ever-growing importance of Nr-red from agricultural sources for Nr deposition in our future scenario.

In addition to the emissions changes of oxidized and reduced forms of Nr, the spatial pattern of Nr deposition responds to future regulations on SO_2 emissions. This is because SO_2 emissions can affect the gas-particle partitioning of Nr species, including NO_x and NH_3 (Nenes et al., 2019; Paulot et al., 2013; Weber et al., 2016). The gas-phase species tend to have much higher deposition velocities than their particle-phase counterparts (Sehmel, 1980). The normalized brute-force sensitivity of total Nr deposition to sulfate concentration is positive in most parts of the central United States with high emissions from agriculture sectors, indicating more localized Nr deposition impacts when less sulfate is available to form particles which tend to be more resistant to deposition (Figure S12). In other words, the SO_2 emission reduction in the future limit the external cost of NH_3 emission through deposition in agricultural intensive regions rather than being exported downwind. However, the magnitude of the sensitivities to a 75% SO_2 emissions reduction is less than 15% in most areas of the CONUS, meaning that further control of SO_2 emissions will affect the spatial pattern of Nr deposition only moderately.

3.3. Comparison Between Nr Deposition and Empirical Lichen-Based CL for Terrestrial Ecosystems

Six of the 10 ecoregions have empirical CLs available based on lichen community composition, including North American Deserts, Mediterranean California, Northern Forests, Northwestern Forested Mountains, Marine West Coast Forest, and Eastern Temperate Forest. The percentage of protected areas with exceedance of CL (referred to exceedance rate hereafter) was high (74–93%) for all the ecoregions except for North American Deserts (Figure 4). The reduction in Nr-ox deposition can reduce the exceedance rate by ~30% in Marine West Coast Forest and Northern Forests to ~60% in Northwestern Forested Mountains and Mediterranean California between 2010 and 2050. The improvements will be largely offset by the additional Nr-red deposition with the expected NH_3 emission increase from agriculture sources in the future. The exceedance rate in Northern Forest will remain high mainly because of the intensified agriculture emissions. The other two ecoregions expect a significant impact from agricultural emission increase are Northwestern
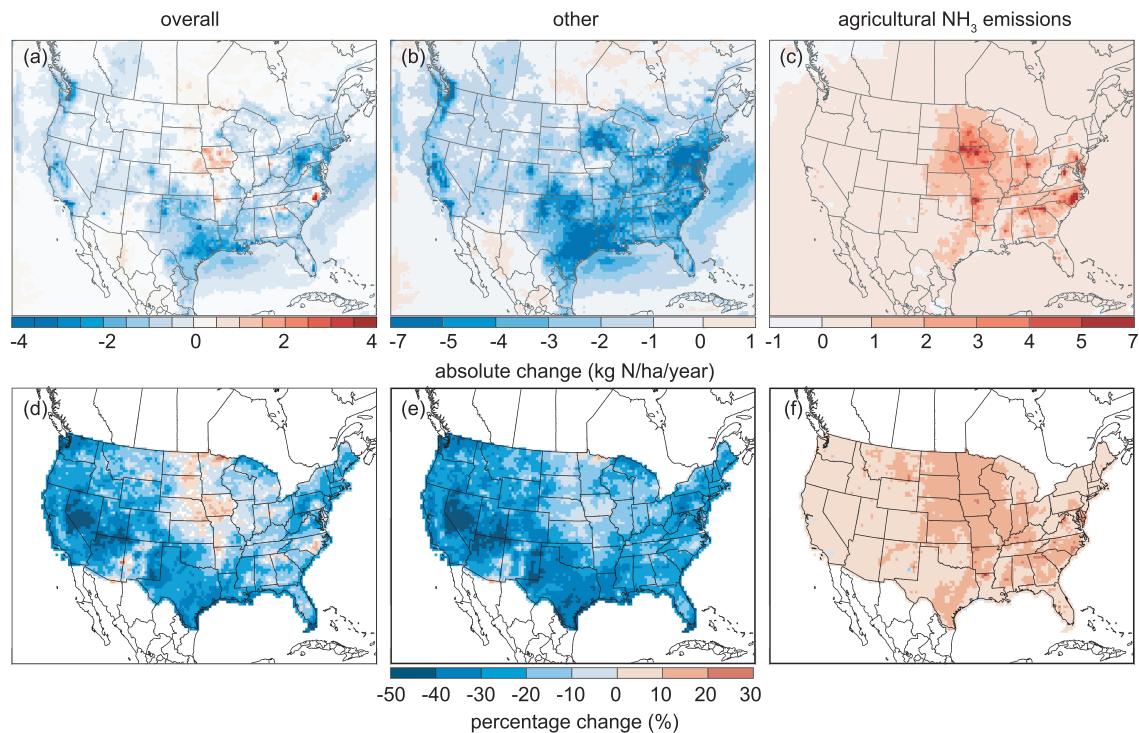
Figure 3. Changes in the spatial distribution of total Nr deposition between 2010 and 2050. (a–c) The absolute change of Nr deposition. (d–f) The percentage change. The overall change between the present-day and future scenario (Ag_projected) (a, d), changes attributable to agricultural NH_3 emissions (b, e), and other factors (c, f) are shown.

Forested Mountains and Eastern Temperate Forest. In particular, the decreasing trend in exceedances in Eastern Temperate Forest will be reversed after 2030 because of the combined increase in Nr-red and Nr-ox deposition. This finding is consistent with the conclusion that most national parks will remain in exceedance in eastern United States in a previous assessment national parks (Ellis et al., 2013).

As Nr-ox deposition further declines, controlling Nr-red deposition becomes even more important to reduce CL exceedances in the future. CL exceedance rate remains high in Northern Forest and Eastern Temperate Forest because of the NH_3 emission increase in the future. The relative contribution of Nr-red to total Nr deposition in these two ecoregions will rise from 48% and 50% in 2010 to 62% and 75% in 2050, respectively. Even if the Nr-ox deposition is zeroed in 2050, the Nr-red deposition will still exceed the CL in 50% and 12% of the sensitive areas, respectively.

3.4. Comparison Between Sulfur-Nitrogen-Combined Deposition and CL Based on Freshwater Acidity and Forest Soil Acidity

Deposited nitrogen and sulfur, together, contribute to the acidity in aquatic and terrestrial ecosystems. In addition to nitric acid deposition, ammonium deposition will also contribute to the acidification with one proton released from the assimilation process or, in rare cases, two protons from the nitrification process if the soil is severely N saturated (Vanbreemen et al., 1982). NH_4^+ deposition was found to have greater ability to increase the modeled surface water acidity in regions with high soil sulfur adsorption capacity (Fakhraei et al., 2016). By aggregating the amount of deposited nitrogen and sulfur, CLs for freshwater acidity and forest soil acidity have been defined as the threshold of the maximum amount of combined sulfur and nitrogen deposition that a sensitive region can tolerate without causing an acidifying effect (Lynch et al., 2017). Speciated Nr deposition fields provide detailed spatial information about the area of concern for exceedances. We focus our discussion on the comparison between deposition and the 10th percentile CL. With substantial reduction of SO_x and NO_x deposition achieved by emission control of fossil fuel combustion under the Clean Air Act (Burns et al., 2011; Greaver et al., 2012), the prevalence of deposition exceedance has already been limited to those most sensitive regions in 2010 (Figure 5). The exceedance rates in
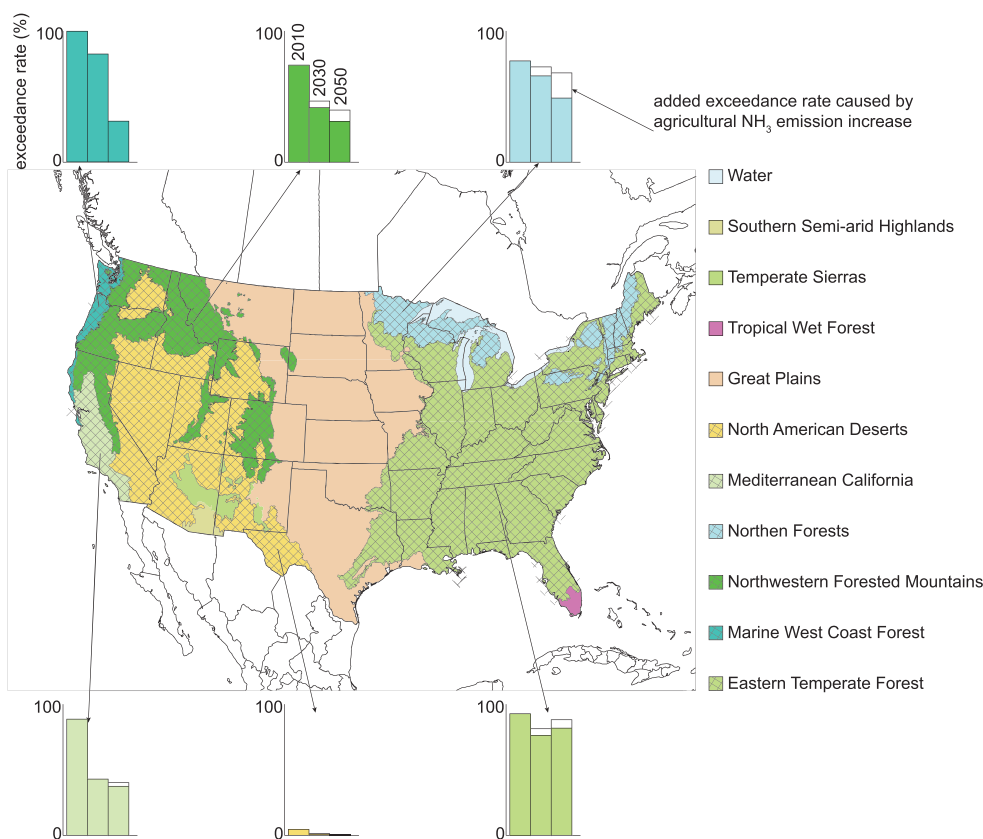
Figure 5. Exceedance of sulfur-nitrogen-combined (S + N) deposition for surface water acidity and forest soil acidity. (a–d) The areas exceeding the 10th percentile CL values for surface water acidity and forest water acidity in 2010 and 2050, respectively. The colors represent the amount of deposition above the 10th percentile CL levels. (e and f) The color-coded maps that show the status of each grid cell in 2050. Gray represents areas with deposition not exceeding the 10th percentile CL values in both 2010 and 2050. Red represents those with deposition in exceedance in both years. Blue represents those with deposition in exceedance in 2010 but below the CL values in 2050. Green represents those with deposition still in exceedance in 2050, particularly because of emission increases from agricultural sources.

importance of mitigating agricultural emissions to protect ecosystem health in adjacent sensitive regions. For surface water acidity exceedances, 11% can be attributed to the same cause, mainly around CAFOs in the southeastern United States. Due to the rising consumption of meat, Nr emissions and discharges from animal industries is expected to pose a greater challenge to the surrounding ecosystems in the future. Mitigating Nr loss from CAFOs relies on a range of measures from implementing the best management

Figure 6. The percentage of sulfur (a and b) and Nr (c and d) deposition required to be deducted to bring sulfur-nitrogen-combined deposition down to the CL levels for surface water acidity (a and c) and forest soil acidity (b and d), respectively.

options available to reduce Nr loss through leaching, runoff, and diffusing to the atmosphere to optimizing feeding plans to reduce nitrogen content in the manure (Carew, 2010; Kohn, 2015). Alternatively, studies point to microbial protein as a food source as the ultimate soluti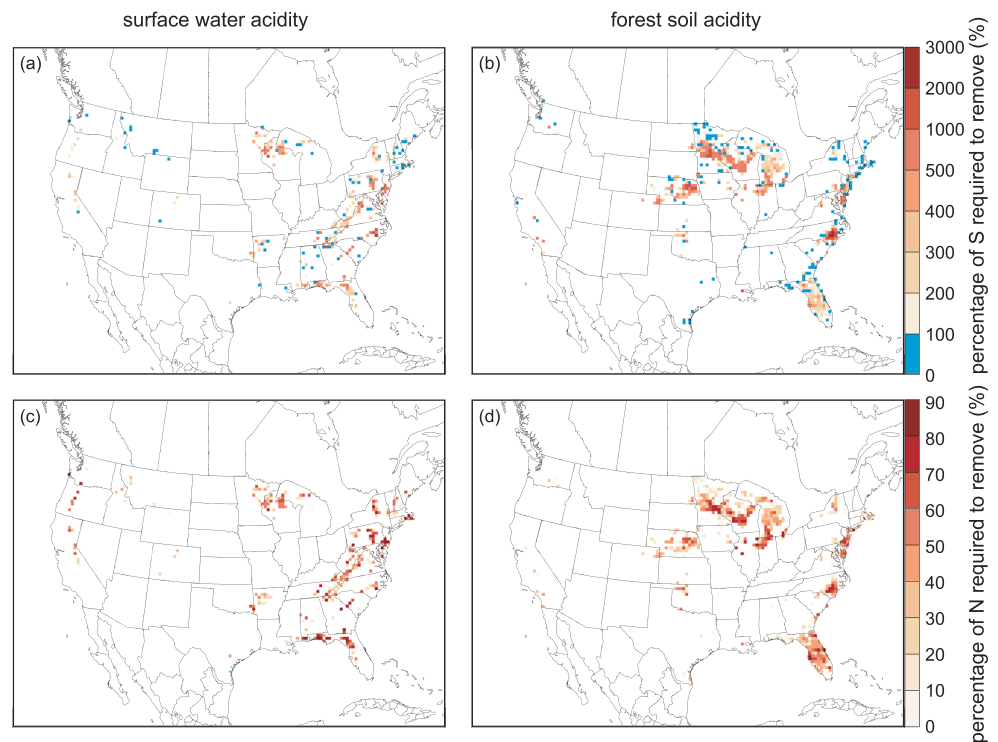on to tackle Nr pollution while sustaining the growing population. (Pikaar et al., 2017, 2018). Results for comparison between deposition level and the average CL are provided in Figure S13.

Acidifying deposition in areas with exceedance can be controlled by individually or simultaneously reducing sulfur and nitrogen deposition. Over the CONUS, reducing sulfur deposition will lead to decreases in the exceedance areas of, at most, 22% and 26% for surface water acidity and forest soil acidity, respectively, in 2050 (Figure 6). In over half of the areas with exceedance, the amount of deposition reduction required to achieve the CL levels is twice as much as the amount of existing sulfur deposition. For areas with intense agriculture production, the required deposition reduction can be up to 30 times that of the sulfur deposition, showing the importance of decreasing Nr species. Given the decreasing trend in sulfur and oxidized-Nr deposition, strategies targeting reduced-Nr deposition from agricultural emissions will become increasingly important to reduce soil and surface water acidification. Such a finding coincides with the conclusion based on site-specific model evaluation that simultaneous reduction of sulfur and nitrogen deposition may be the most effective approach to achieve greatest overall recovery of Adirondack surface water acid neutralizing capacity (Zhou et al., 2015).

3.5. Impact of Nr Atmospheric Deposition on Total Nr Load Received by Watersheds

In addition to atmospheric deposition, the land and water surface also receive Nr input from other sources including Nr runoff from agriculture land, animal farms, and point sources like municipal and industrial facilities (Puckett, 1994). Information about the relative importance of different sources to total Nr loading for areas with CL exceedance is useful in setting priorities of mitigation strategies. By linking the SPARROW model with the simulated Nr deposition, we located the watersheds where atmospheric deposition is the leading Nr source. By contrasting the simulated total Nr loading based on the "Ag_projected" and "Ag_fixed" Nr deposition fields, we estimated the future changes in total Nr loading of 61,117 watersheds

legend:
- urban
- atmospheric deposition
- corn and soybean
- alfalfa
- wheat
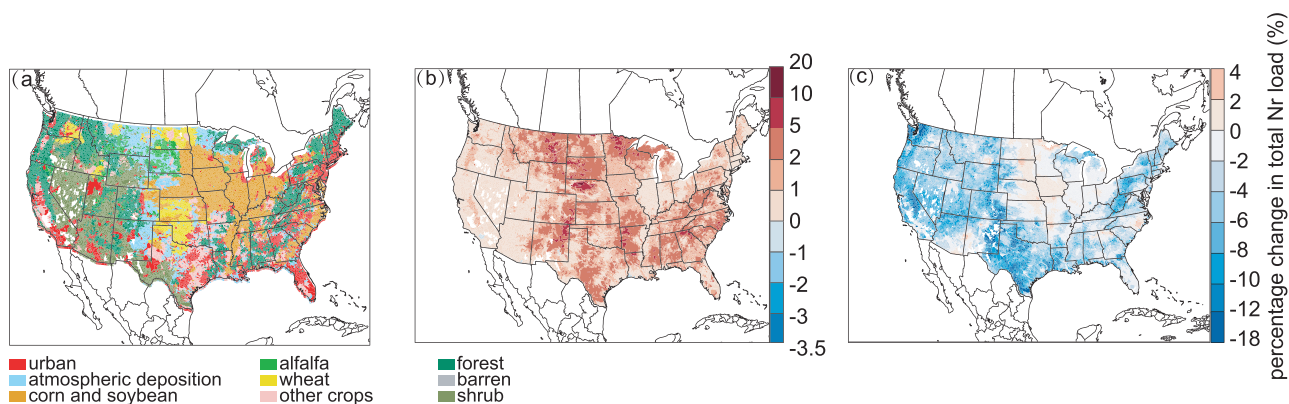- other crops
- forest
- barren
- shrub

Figure 7. Major source of total Nr loading by watershed in "Ag_projected" scenario in 2050 (a). Percentage changes in total Nr loading by watershed across the CONUS due to Nr deposition changes related to agricultural NH_3 emission changes between 2010 and 2050 (b). Percentage changes in total Nr loading due to overall changes in Nr deposition between 2010 and 2050 (c).

nationwide due to the future changes in agricultural NH_3 emissions. It is found that in 2050 under the "Ag_projected" scenario, runoff from agriculture land and municipal sources remain important sources of Nr loading in populated areas. However, atmospheric deposition is the major source of Nr and key for regulation in remote areas with an absence of other significant anthropogenic contributors. Twenty-three percent of the watersheds in the Great Plains region have atmospheric deposition as the major contributor (Figure 7). Surface waterbodies still in exceedance of their CLs within this region include lakes within the Glacier National Park in Montana and lakes within the Indian Peaks wilderness area in Colorado (Figure 5). Another region of concern is the area around the Superior National Forest in Minnesota where the total nitrogen loading in watersheds are sensitive to deposition changes from agricultural sources. The increases in the total Nr loading are estimated to be as high as 5–20%, indicating that Nr emission control on agricultural sources can effectively reduce Nr exceedance in this area. The changes above only address the influence through atmospheric deposition. The overall contribution from agricultural sources through atmospheric deposition, leaching, and runoff is expected to be more significant both in the magnitude and spatial coverage, which warrants further assessment. When Nr deposition changes from all emission sources are incorporated in the SPARROW simulation, the total Nr loads are expected to decrease in 2050 in most of the watersheds, except for the ones in intensive agricultural regions (Figure 7c). The SPARROW simulations in this study employ the same set of model parameters calibrated using monitoring data over CONUS for all regions. Future studies may improve or complement the results by applying the new, nationwide SPARROW models consisting of five regionally calibrated models because the parameters better characterize the local hydrologic and water quality conditions in each region (USGS, 2020).

4. Concluding Remarks

Our analysis shows that NO_x emission reductions coupled with NH_3 emission increases will lead to a transition from an Nr-ox-dominated deposition pattern in 2010 to a Nr-red-dominated pattern in 2050. While Nr deposition is estimated to decrease in most of the CONUS with further NO_x emission control, in agricultural intensive regions the decreasing trend will be offset by rising NH_3 emissions. In addition, increased NH_3 coupled with less nitrate and sulfate aerosol formation leads to more localized deposition. Adding this indirect effect upon the increasing Nr emissions from agricultural sources further increases the Nr burden in near-source regions. This analysis was based upon the $RCP_{8.5}$ + SSP5 pathway, which emphasizes the impact of rising temperatures in the future with continuous dependence on fossil fuels, but still has reductions in NO_x due to controls. Total Nr deposition is expected to be lower under other RCP and SSP scenarios because of reduced fossil fuels use leading to lower NO_x emissions, especially in the eastern CONUS (Ellis et al., 2013). Agricultural NH_3 emission will dominate the Nr deposition in such scenarios. Other future projections, such as a future scenario with a higher adoption rate of biofuels, would likely lead to an even greater

proportion of future Nr deposition from agricultural sources and yield different amounts and spatial patterns of Nr deposition (Duval et al., 2015).

Total Nr deposition is projected to decline by over 20% by 2050, however, comparison between simulated Nr deposition and the empirical CLs for different ecoregions shows that Nr deposition will still exceed CLs in most sensitive areas in Northern Forest and Eastern Temperate Forest partly due to the increase in Nr-red deposition caused by NH_3 emission increase in the eastern United States, indicating the importance to simultaneously reduce NH_3 emissions while controlling NO_x emissions in the future. Without adequate information on ecological impacts for speciated nitrogen deposition, Nr-ox and Nr-red are treated the same when assessing the CL exceedances. As greater contribution from Nr-red deposition is expected in the future, more studies on various ecosystems are need to better understand the ecological impacts of such a shift in deposition toward being Nr-red-dominated.

At present-day level, the percentage of protected areas in exceedances of surface water and forest soil acidity is 16% and 22%, respectively, much lower than that of lichen-based empirical CL (52%), similar to the findings in Europe (Hettelingh et al., 2007). Comparison between present-day and future simulations shows a significant reduction in exceedance rates nationwide between 2010 and 2050 (~50% reduction in both surface water CL exceedances and forest soil CL exceedances for acidity), mainly achieved by a reduction in Nr-ox deposition in the future when NO_x emissions are further controlled. However, increased emissions from agricultural sources contribute oppositely to deposition reduction. We estimate that the increase in agricultural emissions between 2010 and 2050 increase the exceedance areas by 22% and 11% for forest soil acidity and freshwater acidity, respectively, which would, otherwise, return their Nr deposition to levels below CLs. The impacted regions mainly locate in areas with intense fertilizer application or hosting CAFO. We also show that atmospheric deposition is the leading contributor to total Nr load in remote watersheds where there is an absence of direct anthropogenic disturbance, including several lakes in National Parks and National Wilderness areas in Colorado, Montana, and Minnesota. Our study highlights the need to better manage diffusive Nr emissions from agricultural sources for the health of aquatic and terrestrial ecosystems under the stress of a warming climate and growing food production in the future.

Data Availability Statement

All data used in this study are publicly available. Data sources are described in section 2.

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