2018

On-road emissions of ammonia: An underappreciated source of atmospheric nitrogen deposition

Mark E. Fenn
USDA Forest Service, mfenn@fs.fed.us

Andrzej Bytnerowicz
USDA Forest Service

Susan L. Schilling
USDA Forest Service

Dena M. Vallano
University of California, Santa Cruz

Erika S. Zavaleta
University of California, Santa Cruz

See next page for additional authors

Science of the Total Environment 625 (2018) 909–919

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

On-road emissions of ammonia: An underappreciated source of atmospheric nitrogen deposition

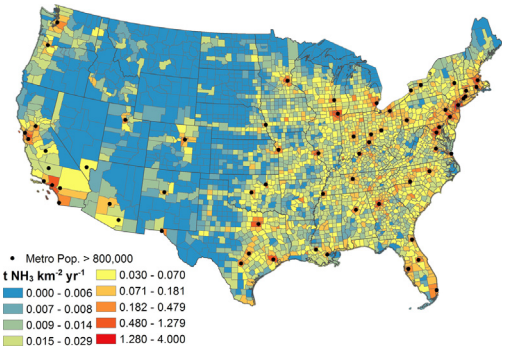
Mark E. Fenn [a,*], Andrzej Bytnerowicz [a], Susan L. Schilling [a], Dena M. Vallano [b], Erika S. Zavaleta [b], Stuart B. Weiss [c], Connor Morozumi [b], Linda H. Geiser [d], Kenneth Hanks [a]

[a] USDA Forest Service, Pacific Southwest Research Station, 4955 Canyon Crest Drive, Riverside, CA 92507, USA
[b] Environmental Studies Department, University of California, Santa Cruz, CA 95064, USA
[c] Creekside Center for Earth Observations, Menlo Park, CA 94025, USA
[d] U.S. Forest Service, Watershed, Fish, Wildlife, Air & Rare Plants, 201 14th Street SW, Washington, DC 20250, USA

HIGHLIGHTS

- This study documents the increasing importance of on-road emissions of NH_3.
- NO_x emissions control mechanisms frequently result in NH_3 production and emissions.
- NH_3 is an important driver of N deposition in urban-affected areas and near roadways.
- NH_4-N:NO_3-N ratios in urban deposition are indicative of elevated NH_3 emissions.
- On-road NH_3 emissions exceed agricultural emissions where 40% of the U.S. resides.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 October 2017
Received in revised form 26 December 2017
Accepted 27 December 2017
Available online xxxx

Editor: Elena Paoletti

Keywords:
Three-way catalytic converter
Nitrogen form
Transport sector
Heavy-duty vehicles
Emissions trends
Urban air pollution

ABSTRACT

We provide updated spatial distribution and inventory data for on-road NH_3 emissions for the continental United States (U.S.) On-road NH_3 emissions were determined from on-road CO_2 emissions data and empirical NH_3:CO_2 vehicle emissions ratios. Emissions of NH_3 from on-road sources in urbanized regions are typically 0.1–1.3 t km^{-2} yr^{-1} while NH_3 emissions in agricultural regions generally range from 0.4–5.5 t km^{-2} yr^{-1}, with a few hotspots as high as 5.5–11.2 t km^{-2} yr^{-1}. Counties with higher vehicle NH_3 emissions than from agriculture include 40% of the U.S. population. The amount of wet inorganic N deposition as NH_4^+ from the National Atmospheric Deposition Program (NADP) network ranged from 37 to 83% with a mean of 58.7%. Only 4% of the NADP sites across the U.S. had <45% of the N deposition as NH_4^+ based on data from 2014 to 2016, illustrating the near-universal elevated proportions of NH_4^+ in deposition across the U.S. Case studies of on-road NH_3 emissions in relation to N deposition include four urban sites in Oregon and Washington where the average NH_4-N:NO_3-N ratio in bulk deposition was 2.3. At urban sites in the greater Los Angeles Basin, bulk deposition of NH_4-N and NO_3-N were equivalent, while NH_4-N:NO_3-N in throughfall under shrubs ranged from 0.6 to 1.7. The NH_4-N:NO_3-N ratio at 7–10 sites in the Lake Tahoe Basin averaged 1.4 and 1.6 in bulk deposition and throughfall, and deposition of NH_4-N was strongly correlated with summertime NH_3 concentrations. On-road

* Corresponding author.
E-mail address: mfenn@fs.fed.us (M.E. Fenn).

https://doi.org/10.1016/j.scitotenv.2017.12.313
0048-9697/Published by Elsevier B.V.

emissions of NH_3 should not be ignored as an important source of atmospheric NH_3, as a major contributor to particulate air pollution, and as a driver of N deposition in urban and urban-affected regions.

Published by Elsevier B.V.

1. Introduction

Increasingly, both agricultural and transport sector emissions of NH_3 have been recognized as important sources of reduced N (Xing et al., 2013), although in some large-scale analyses only agricultural sources are considered (Battye et al., 2017; Moldanová et al., 2011; Pye et al., 2009). Estimated emissions of NH_3 in the United States increased by 91, 70 and 7% in the on-road, power plant and agricultural sectors, respectively, between 1990 and 2010 (Xing et al., 2013). Emissions of NH_3 from motor vehicles (Kean et al., 2009; Leip et al., 2011) and industrial stacks (Hertel et al., 2011; Li et al., 2017; Vallero, 2014) are largely a byproduct of stringent NO_x control technologies. In many regions of the developed world, NO_x emissions have steadily declined since around 1990 (Leip et al., 2011) while emissions of NH_3 have remained constant or increased slightly, such as in the United States where NH_3 emissions have increased by 11% (Bytnerowicz et al., 2016; Hertel et al., 2011; Xing et al., 2013). As a result, the proportion of N deposition in reduced forms in many areas of the developed world, has increased in recent years (Du et al., 2014; Hůnová et al., 2017; Li et al., 2016).

Light and medium duty motor vehicles equipped with three-way catalytic converters dominate our roadways and produce NH_3 (Bishop and Stedman, 2015). As a result of the introduction of more stringent standards for emissions of NO_x and particulate matter in California, nationwide by the U.S. Environmental Protection Agency (USEPA), and in Europe (Hertel et al., 2011; Leip et al., 2011) heavy-duty vehicles now include a mix of natural gas engines with three-way catalytic converters and diesel engines equipped with selective catalytic reduction (SCR). In SCR, which is also used in light-duty diesel powered cars and fleet vehicles, aqueous urea is injected as a reductant for NO_x control, resulting in production of NH_3 (Bishop and Stedman, 2015; Thiruvengadam et al., 2016). Heavy duty vehicles, including city buses, refuse trucks, cargo vehicles, and clean diesel trains equipped with current emissions control technology are becoming an increasingly important source of NH_3 emissions in urban areas and along transport corridors.

Air-fuel ratios that are slightly rich result in maximal NO_x reductions, yet are the most conducive to NH_3 production from three-way catalytic converters (Thiruvengadam et al., 2016). Therefore a trade-off exists whereby conditions favoring NO_x reduction generally favor NH_3 production by three-way catalytic converters (Heeb et al., 2006). As a result of NH_3 production from NO_x control mechanisms, urban areas may represent more important NH_3 emissions source areas for downwind ecosystems than commonly recognized, particularly as urbanization continues to expand its footprint. Livingston et al. (2009) argue that broad scale emissions inventories of NH_3 "fail to take into account the spatial distribution of ammonia emissions and the potential for relatively high emissions from mobile sources in dense, highly urbanized airsheds".

This study builds on the work of Du et al. (2014) and Li et al. (2016) who demonstrated the increasing importance of reduced forms of N deposition in the U.S., and the work of Sun et al. (2017) who describe an improved method for estimating on-road emissions of NH_3. The overarching objective of this analysis is to evaluate the increasing importance of reduced forms of reactive N in areas influenced by urban and on-road emissions. More specifically, the supporting objectives of this study are three-fold: (1) to provide national scale on-road NH_3 emissions data and spatial patterns; (2) to compare temporal trends in NO_3^- and NH_4^+ wet deposition in sites primarily affected by urban versus agricultural emissions; and (3) to present case studies of regional-scale empirical deposition and atmospheric exposure data showing the contribution of on-road NH_3 emissions towards elevated atmospheric N exposure and deposition in urban and urban-influenced ecosystems.

2. Methods

2.1. Ammonia emissions data

Agricultural and on-road emissions of NH_3 are from the 2014 USEPA National Emissions Inventory (NEI; USEPA, 2017). Downloaded NH_3 data was aggregated by the sector: "Agriculture" (Crops and Livestock Dust, Fertilizer Application, and Livestock Waste) and the Tier 1 category "Highway Vehicles". Emissions of NH_3 were also estimated based on vehicular CO_2 emissions and well-documented on-road NH_3:CO_2 emissions ratios (summarized in Sun et al., 2017). This ratio approach is considered to be a robust method for estimating on-road NH_3 emissions because the uncertainty in on-road CO_2 emissions is much less than for estimates of on-road NH_3 emissions (Sun et al., 2017). On-road CO_2 emissions used to calculate on-road NH_3 emissions were obtained from the Database of Road Transportation Emissions (DARTE) (DARTE, 2017; Gately et al., 2015; USEPA, 2017). DARTE is an annual 1-km grid of CO_2 emissions from 2012 using the Federal Highway Administration's Highway Performance Monitoring System roadway-level vehicle miles travelled and state data. The data are available as a GeoTiff, ESRI geodatabase, and comma-separated (text) file. Data includes annual estimates of CO_2 emissions in megagrams (metric tons) for the years 1980–2012. In ArcGIS, the DARTE 1-km polygon grid was intersected with the US Census county map (U.S. Census Bureau, 2017; ftp://ftp2.census.gov/geo/tiger/TIGER2016/COUNTY/tl_2016_us_county.zip; accessed 4/10/2017). Megagrams of CO_2 emitted in 2012 were summed by county and exported to Excel for further calculations. County totals of CO_2 in metric tons were converted to metric tons of NH_3 using the Sun et al. (2017) error-weighted average NH_3:CO_2 ratio of 0.42. This ratio value is based on a synthesis of studies in the U.S. and is also consistent with studies in Europe. The NH_3:CO_2 emission ratio is calculated as ppbv NH_3:ppmv CO_2 (Sun et al., 2017). As noted, the NEI NH_3 emissions data used in our analysis are from 2014, the most recent available, while the CO_2 emissions from DARTE are from 2012, also the most recent data available. Thus, this two-year differential adds uncertainty to the estimates—but these are the best data available for this analysis.

2.2. Wet deposition trends in sites influenced by urban and agricultural emissions

Ionic concentration wet deposition data were downloaded from the National Atmospheric Deposition Program, National Trends Network (NADP/NTN) website (http://nadp.sws.uiuc.edu/ntn/). Data were selected from eight sites primarily affected by agricultural emissions and eight sites primarily influenced by urban emissions. Urban influenced sites were selected based on proximity (<7 km) to urban areas delineated in U.S. Census Bureau data (U.S. Census Bureau, 2017; ftp://ftp2.census.gov/geo/tiger/TIGER2016/UAC/tl_2016_us_uac10.zip; accesssed 4/10/2017). Agricultural sites were selected if surrounding land use, according to NLCD 2011 land cover database, was primarily cultivated crops or pasture (Homer et al., 2015; U.S. Geological Survey, NLCD 2011 Land Cover (2011 Edition, amended 2014) - National Geospatial Data Asset (NGDA) Land Use Land Cover, http://www.mrlc.gov, accessed August 2017). The data were converted to $\mu eq\ L^{-1}$ units, plotted and linear regression lines were added. The location of the NADP monitoring site downwind of Portland, Oregon (OR98) was moved in

2003 from the Oregon side of the Columbia River Gorge to the Washington (WA98) side of the Gorge. Concurrent monitoring for the years 2002–2003 confirmed that deposition at the two sites was highly similar (http://nadp.sws.uiuc.edu/ntn/).

As an update on proportional wet deposition as NH_4-N in the contiguous U.S. (CONUS) we followed the procedure of Li et al. (2016) in calculating percent wet inorganic N deposition as NH_4^+ from the NADP/NTN. Isopleths were produced by interpolating NH_4-N percentages at individual monitoring sites using a cubic inverse-distance weighting of sites. Annual monthly precipitation weighted mean concentration data were downloaded (June 5, 2017) from http://nadp.sws.uiuc.edu/data/ntn/. Values for NH_4^+ and NO_3^- were converted to unit N and the percent deposition as NH_4^+-N was calculated (NH_4^+-N/(NH_4^+-N + NO_3^--N) * 100). Annual values were excluded if NADP criteria 1 (completeness of data defined as percentage of the monitoring period for which there are valid samples) was <75% for the year. Valid annual values for the years 2014–16 were averaged. Sites with fewer than 2 of the 3 years of valid data were excluded except the two North Dakota sites (ND00, ND11) and one site in Washington (WA98). Of the 254 active NADP sites in CONUS, 227 were used in this analysis. An interpolated surface was generated using ESRI Geostatistical Analyst Inverse Distance Weighting method, power = 3, using a minimum number of neighbors of 10 and maximum number of neighbors of 15.

2.3. Case studies

2.3.1. Passive sampler measurements of atmospheric concentrations

Two-week average concentrations of gaseous nitrogenous pollutants were measured during the summer dry season using passive samplers for nitric acid vapor (HNO_3), nitrogen dioxide (NO_2), nitrogen oxides (NO_x) and ammonia (NH_3). Ammonia, NO_2 and NO_x were measured with Ogawa samplers (Fenn et al., 2009; Ogawa, and Company, USA, Inc., 2006; Roadman et al., 2003). Nitric acid was measured with nylon filter type samplers (Bytnerowicz et al., 2005). This passive sampler monitoring was done from 2005 to 2014 at three sites: Tanbark Flat on the eastern edge of greater Los Angeles; Camp Paivika, a highly-polluted forested site on the western edge of the San Bernardino Mountains located about 80 km east of Los Angeles, and the Santa Margarita Ecological Reserve, 60 km south of Riverside, California (Fig. 1). Passive samplers were also deployed at a network of ten sites within the Lake Tahoe Basin in the summer of 2010.

Ogawa passive samplers for NO_x, NO_2 and NH_3 were also deployed in 2002 and 2010 at three serpentine grassland sites along the coastal San Francisco peninsula in the San Francisco/San Jose area. The Edgewood County Park site (EW) is south of San Francisco near Highway 280. At Edgewood, passive samplers were placed at 50 m and 530 m from the highway and are referred to as the near and far sites. At the Coyote Ridge (CR) site south of San Jose, passive samplers were located at 300 and 1500 m from the highway. The third monitoring site was the Jasper Ridge Biological Preserve (JR), which is not adjacent to a highway. Passive samplers were only deployed at one location at JR.

2.3.2. NH_4-N:NO_3-N ratios in deposition

Ratios of NH_4-N:NO_3-N in bulk deposition, and in some locations in throughfall, were calculated at a number of urban-affected sites in California, Oregon, Washington and at ten sites in the Lake Tahoe Basin located in northern California, near the border with the state of Nevada. Deposition fluxes were measured using ion exchange resin collectors which capture ions from solution as they percolate through the resin column (Fenn and Poth, 2004). Throughfall was collected under chaparral and coastal sage scrub vegetation at sites within several southern California counties. Bulk deposition was also measured at four urban locations in the states of Oregon and Washington from July 2007 to July 2008. An interpolated surface was generated from the chaparral and coastal sage scrub throughfall data using ESRI Geostatistical Analyst Inverse Distance Weighting method, power = 2.

3. Results

3.1. Ammonia emissions sources in CONUS

Comparisons of NH_3 emissions from on-road sources with those from agriculture across the U.S. are shown in Fig. 2. As expected, elevated NH_3 emissions from agriculture are more widespread and are dominant in the Midwest region and in a few isolated hotspots; Agricultural emissions reach higher levels in the most affected counties compared to on-road emissions. Extensive portions of the Southeast and Northeast regions of the U.S. receive high proportions of the total NH_3 emissions from urban sources, and in much of this region agricultural emissions are relatively low. The interior West is a mosaic of regions characterized by low NH_3 emissions interspersed with regions of either elevated urban/on-road emissions or agricultural emissions of NH_3. A few counties in hotspots of agricultural emissions in California, Iowa,

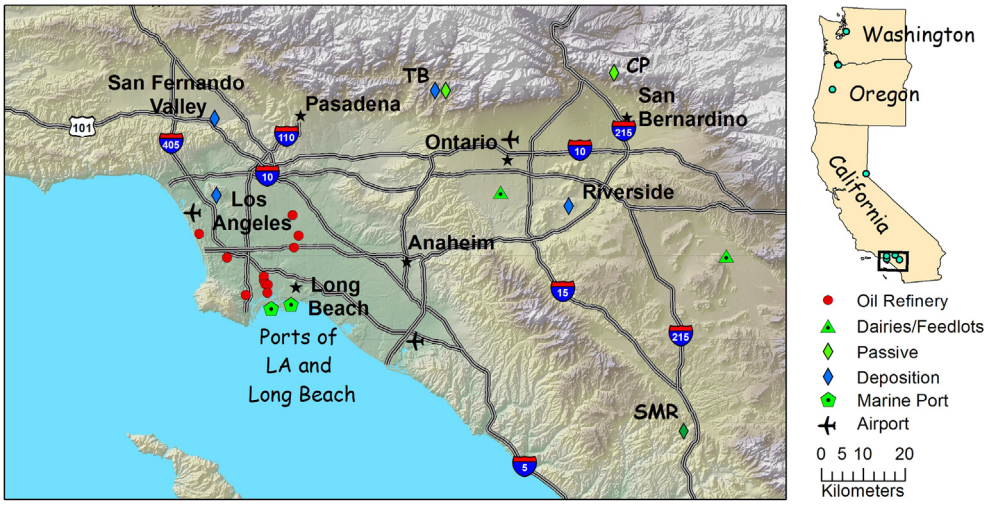


Fig. 1. Map showing bulk deposition (Deposition) monitoring sites in the Los Angeles (LA) Air Basin. Passive air samplers (Passive) were deployed at three sites: Camp Paivika (CP) in the San Bernardino Mountains; Tanbark Flats (TB) in the San Gabriel Mountains; Santa Margarita Ecological Reserve (SMR) located west of Interstate 15 at the SE portion of the study area in the foothills of the Santa Ana Mountain Range. The inset map shows locations of deposition sites in the states of Washington and Oregon, and the Lake Tahoe area in northeastern California, bordering on Nevada.

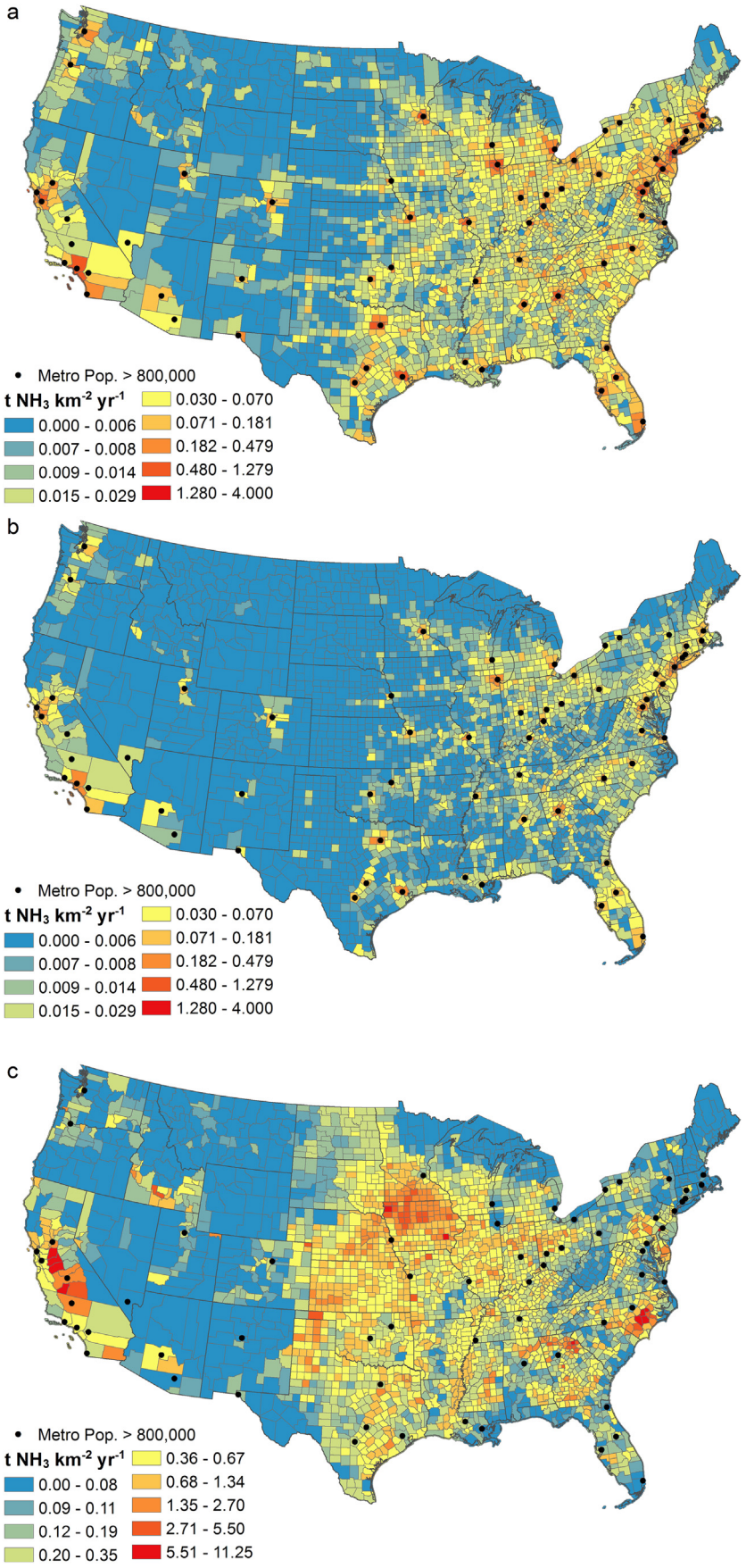


Fig. 2. County-level on-road emission fluxes of NH_3 based on DARTE CO_2 on-road emissions for 2012 and published NH_3:CO_2 mobile-source emissions ratios (a), from the USEPA NEI for 2014 (b), and agricultural emissions from the USEPA NEI for 2014 (c). Note difference in scale for the agricultural emissions fluxes. Circles represent metropolitan areas with a population of 800,000 or greater in 2010. See text for methodological details.

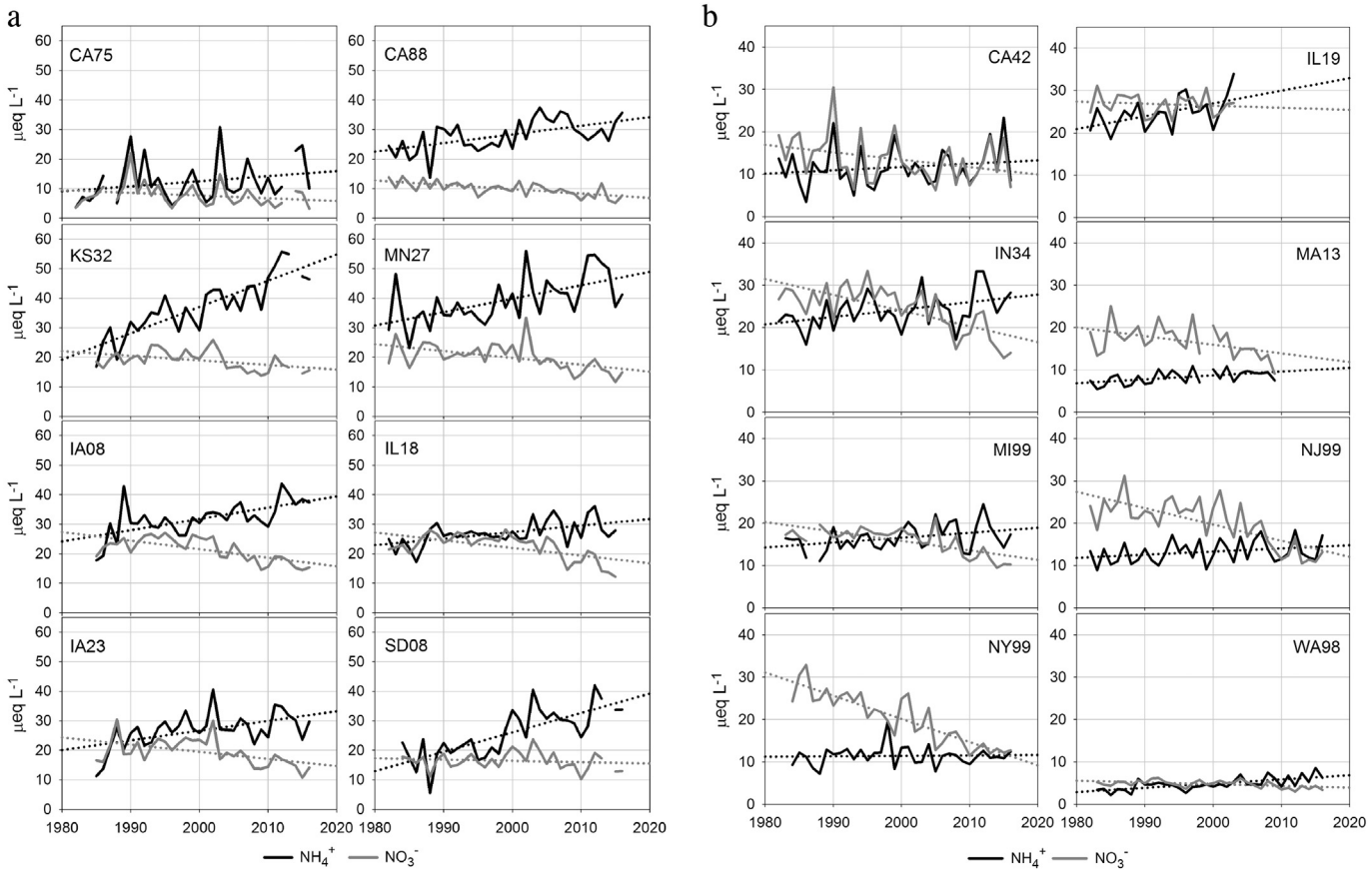


Fig. 3. Temporal trends in concentrations of NH_4^+, NO_3^- and SO_4^{2-} in wet deposition at eight NADP/NTN sites primarily affected by agricultural emissions (a) or urban emissions (b). Note different y-axis scales in Fig. 3a and b.

Georgia, North Carolina and Pennsylvania had NH_3 emissions ranging between 5.1 and 11.2 t km^{-2} yr^{-1}. The maximum annual NH_3 emissions estimated for agricultural and on-road dominated areas were 11.2 and 3.4 t km^{-2}, respectively. Emissions were most commonly in the range of 0.4 to 5.5 t km^{-2} yr^{-1} in agricultural areas (Fig. 2). By comparison, in major urban areas on-road emissions of NH_3 were typically in the range of 0.03 to 1.3 t km^{-2} yr^{-1}.

Based on the NEI emissions data, there were 200 counties for which at least 33% of the emissions originate from on-road sources. In contrast, based on the CO_2 emissions approach, 440 counties are characterized by

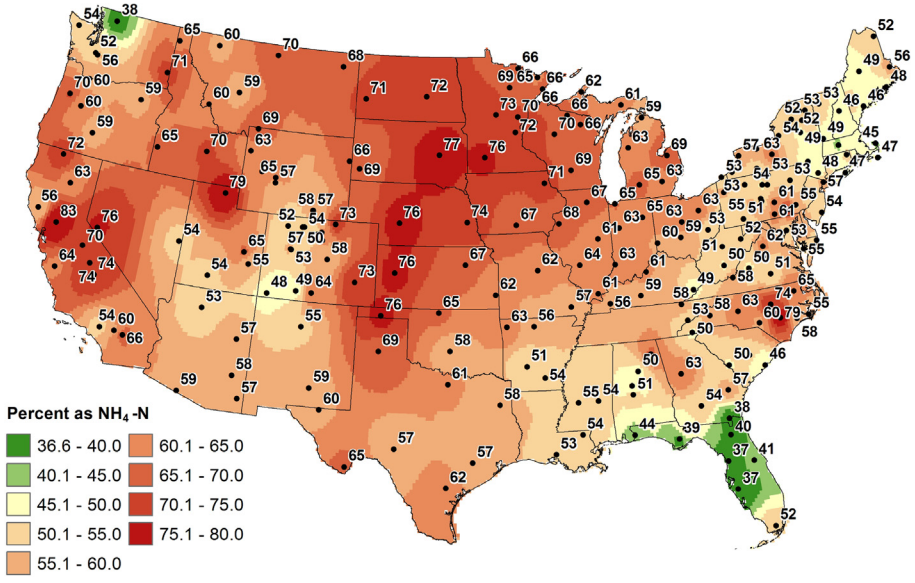


Fig. 4. Three-year average percentage of wet inorganic nitrogen deposition as NH_4-N across the United States from 2014 to 2016. The black dots on the map represent locations of sites with three years of data available. The NH_4^+ percentage on a molar basis is noted at each site.

at least one-third of the NH_3 emissions from on-road sources. In 2014 annual emissions of NH_3 in the CONUS from on-road sources were 3.2% of total emissions (defined as on-road + agricultural emissions) based on data from the NEI (0.09 Tg yr^{-1}). Estimates were much higher at 8.2% of total emissions in 2012 (0.26 Tg yr^{-1}) based on the DARTE CO_2 emissions approach we are using in this study. Thus, our estimates of on-road NH emissions in the CONUS are 2.9-fold greater than indicated in the NEI.

3.2. Temporal trends in NO_3^- and NH_4^+ concentrations in wet deposition at selected urban- and agricultural-dominated sites, and percent of wet N deposition as NH_4^+ in the CONUS

At all 16 sites shown in Fig. 3, whether predominantly affected by urban or agricultural emissions, NO_3^- concentrations are declining. Mean decreases for NO_3^- concentrations were 0.17 and 0.25 μeq L^{-1} yr^{-1} for agricultural and urban sites (respective ranges: 0.04–0.29 and 0.04–0.55). All of the agriculturally-influenced sites show a strong increasing trend in NH_4^+ deposition (0.17–0.89 μeq L^{-1} yr^{-1}; mean = 0.48). The urban sites show a slightly increasing trend of NH_4^+ deposition (from 0.01–0.30 μeq L^{-1} yr^{-1}; mean = 0.12; Fig. 3). At six of the eight urban sites NH_4^+ concentrations reached values ≥ NO_3^- concentrations during the 2005–2010 time period. The exceptions were the Chicago (IL19) and New York City (NY99) sites where NH_4^+ concentrations reached similar levels as NO_3^- in 2001 and 2016, respectively (Fig. 3).

Within CONUS the percent of wet inorganic N deposition as NH_4^+ ranged from 37 to 83% with a mean of 58.7%. Only 4% of the NADP sites across the U.S. had <45% of the N deposition as NH_4^+ based on data from 2014 to 2016 (Fig. 4), illustrating the near-universal occurrence of relatively high NH_4^+ deposition across the United States.

3.3. Case studies

3.3.1. Passive sampler measurements of atmospheric concentrations

At three sites in the Los Angeles Basin, NH_3 concentrations remained relatively unchanged from 2005 to 2014 (missing data in 2011; Fig. 5). Concentrations of oxidized gaseous N compounds show a clear declining pattern over this same period. As a result, NH_3:NO_y ratios (NO_y = sum of NO, NO_2 and HNO_3) increased during the monitoring period. Concentrations of HNO_3 and NO_2 (data not shown) were greatest at Tanbark and the ratio of NH_3-N:HNO_3-N, the two N compounds with the highest deposition velocities (Zhang et al., 2009), was lowest at Tanbark with a ratio of 1.5 compared to 2.3 and 3.7 at Camp Paivika and Santa Margarita, respectively (Fig. 5).

On average, NH_3 concentrations at the coastal San Francisco peninsula sites shown in Fig. 6 were 4.7 times higher in 2010 than in 2002. The only site that did not show an increase in NH_3 concentrations in 2010 was the Edgewood near site (50 m from the highway). In contrast the Edgewood far site (530 m from the highway) showed a 4.7-fold increase in NH_3 concentrations in 2010. By comparison, NO and NO_2 concentrations decreased by 50% and 35% on average for the five monitoring sites. Concentrations of NO_x (NO-N + NO_2-N) declined on average among the five sites by 41% from 2002 to 2010 (Fig. 6).

3.3.2. NH_4-N:NO_3-N ratios in deposition

In four urban sites in Oregon and Washington the NH_4-N:NO_3-N ratio averaged 2.3 in bulk deposition (range of 1.8–2.9) in open canopy-free areas (Table 1). Ratios of NH_4-N:NO_3-N in bulk deposition in the Los Angeles Basin were lower than in the cities in Oregon and Washington (average = 1.0; range of 0.9–1.3). Ratios of NH_4-N:NO_3-N in throughfall in southern California shrub lands ranged from 0.7 to 1.5 across a more spatially extensive network of chaparral and coastal sage scrub sites with high but varying degrees of urban influence (Fig. 7).

Annual deposition of N (NO_3-N + NH_4-N) in throughfall at ten sites in the Tahoe Basin ranged from 1.7 to 5.6 kg ha^{-1} yr^{-1} compared 1.0 to 3.0 kg N ha^{-1} yr^{-1} in bulk deposition (7 sites). The site with the highest summertime average NH_3 concentration (2.1 μg m^{-3}) and the highest annual throughfall deposition of NH_4-N was Valhalla (3.6 kg ha^{-1} yr^{-1}), the site closest to the city of South Lake Tahoe and just off the main highway. The NH_4-N:NO_3-N ratio at the sites averaged 1.4 and 1.6 in bulk deposition and throughfall, respectively. The ratio in throughfall at Valhalla was 1.9. Annual throughfall and bulk deposition of NH_4-N was strongly correlated with summertime NH_3 concentrations (R^2 = 0.90 for throughfall and 0.83 for bulk deposition) in the Lake Tahoe Air Basin.

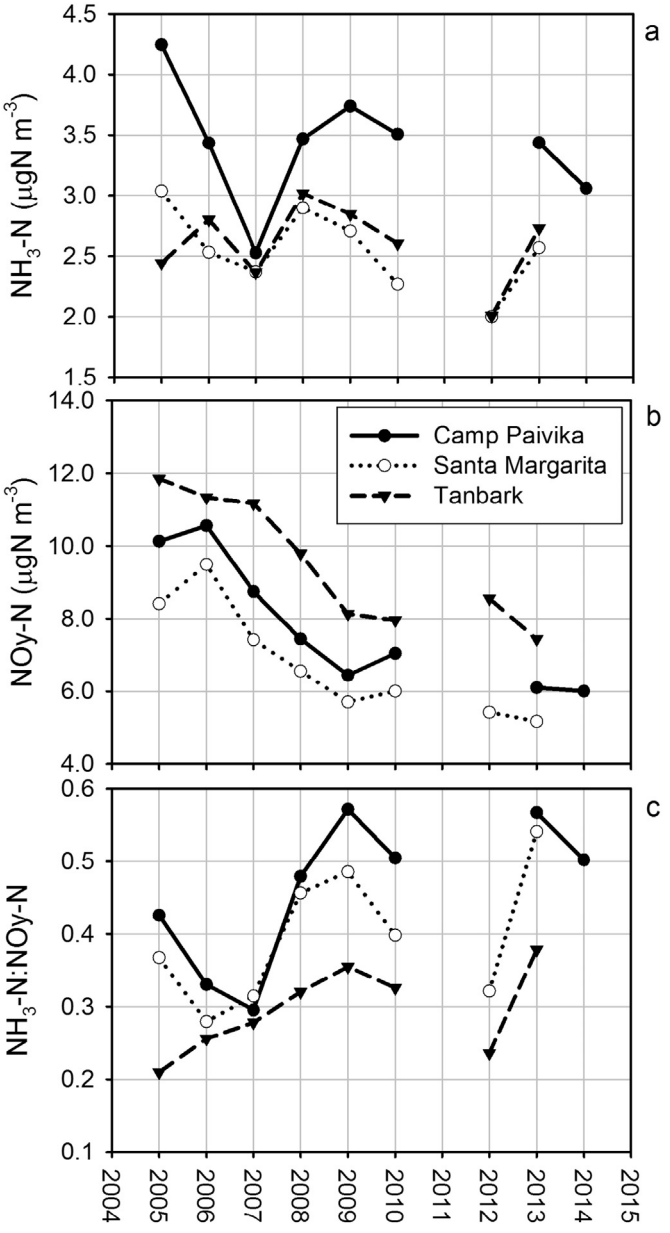


Fig. 5. Temporal trends in summertime concentrations of NH_3-N and NO_y-N and in the NH_3-N:NO_y-N ratio at three sites in the Los Angeles Air Basin.

4. Discussion

The improved national scale estimates of on-road NH_3 emissions reported herein show that areas with elevated on-road NH_3 emissions are widespread in the eastern half of the U.S., along the west coast, and across urbanized regions of the interior West. This spatial extensiveness

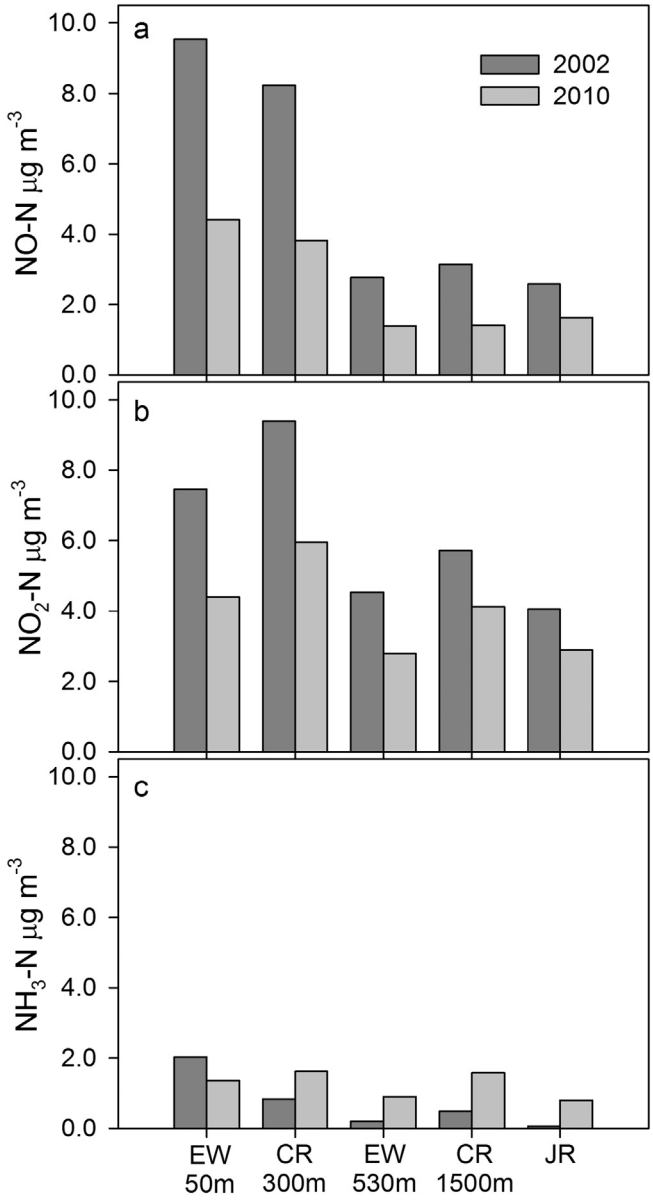


Fig. 6. Concentrations of NO-N (a), NO_2-N (b) and NH_3-N (c) in 2002 and 2010 at three locations in the San Francisco Bay area. Values represent annual averages based on 12 monthly exposures. At Edgewood (EW) passive samplers were placed at 50 m and 530 m from the highway and at Coyote Ridge (CR) samplers were located at 300 and 1500 m from the highway and referred to as near and far sites, respectively. At the Jasper Ridge Biological Preserve (JR) samplers were deployed in one location that was not adjacent to a highway.

of elevated on-road NH_3 emissions is also evident by the fact that 440 counties across the U.S. receive at least one-third of their NH_3 emissions from on-road sources. The universal and increasing importance of reduced forms of N deposition is also seen in the elevated proportions of N wet deposition occurring as NH_4-N across the U.S. (NADP data from 2014 to 2016 at 227 sites). Temporal trends in wet deposition indicate increasing NH_4-N and decreasing NO_3-N since the mid 1980s at 16 NADP sites primarily affected by either agricultural or urban/on-road emissions. Atmospheric NH_3 data and NH_4-N:NO_3-N ratios in bulk deposition and throughfall at urban and urban-influenced sites in the states of Washington, Oregon and California confirm the importance of on-road emissions of NH_3 in affecting air quality and as an important driver of N deposition in urban and urban-affected ecosystems. In summary, these findings suggest that effective NO_x emissions controls from the transport sector result in reduced NO_x emissions and NO_3-N deposition but also result in increased on-road production and emissions of NH_3 which then contributes to NH_4-N deposition and increased NH_4-N:NO_3-N ratios in atmospheric deposition. These salient points are discussed in greater detail below in Sections 4.1 to 4.4.

4.1. Magnitude of agricultural and on-road emissions of NH_3

As expected, agricultural emissions are the largest source of NH_3 emissions nationwide. This agricultural signal is evident from emissions inventories, and also from the NADP nationwide network of wet deposition which shows many sites in the major agricultural regions in the Midwest and in central California where NH_4^+ deposition constitutes 65 to 77% or more of the wet deposition of inorganic N. We identified eight NADP sites located adjacent to urban source regions with little known agricultural influence, and yet the percent N deposition as NH_4^+ in these sites still ranges from 43 to 65%. The NADP data show that sites within major agricultural regions have experienced stronger increases in wet deposition NH_4^+ concentrations over time (0.17–0.89 μeq L^{-1} yr^{-1}), compared to urban-affected sites where NH_4^+ has been increasing only gradually (0.01–0.30 μeq L^{-1} yr^{-1}).

At 96% of the NADP sites, at least 45% of the DIN deposition was in the form of NH_4-N during 2014–2016 and the average for all the sites was 58.7%. Even though the NADP primarily locates sites in rural areas, many sites are surrounded by on-road and urban sources, and therefore non-agricultural sites also show deposition with relatively high percent deposition as NH_4^+. This near universal pattern of proportionally high NH_4^+ deposition across the NADP network supports the conclusion that agriculture is not the only important source of NH_4^+ in the U.S.

The relative importance of agricultural emissions versus urban or on-road emissions of NH_3 varies across the landscape. In some regions both sources are important, particularly in regions of mixed land use, such as Denver and Los Angeles (Sun et al., 2017). The eastern portions of the Los Angeles Air Basin are strongly influenced by mobile sources

Table 1
Annual bulk (open-site) nitrogen deposition and NH_4-N:NO_3-N ratios in urban areas of Oregon, Washington and California.

Study site	NO_3-N	NH_4-N	NH_4-N:NO_3-N	Location
City of Portland, Forest Park	0.94	2.10	2.2	Portland, OR
City of Portland, Oregon Zoo	1.45	4.27	2.9	Portland, OR
City of Eugene, Hendricks Park	0.52	1.19	2.3	Eugene, OR
City of Seattle, Seward Park	0.94	1.73	1.8	Seattle, WA
Lake Tahoe Basin (7 sites)	0.58	0.81	1.4	Northern California
Tanbark[a]	1.54	1.50	1.0	Los Angeles CA Air Basin
Riverside[b]	1.36	1.73	1.3	Los Angeles CA Air Basin
Central Los Angeles[c]	1.69	1.52	0.9	Los Angeles, CA
San Fernando Valley[c]	1.57	1.39	0.9	Los Angeles, CA

[a] Average of 4 years: Fall 2009–Fall 2013; Data missing for Summer 2012.
[b] One year: Spring 2011–Spring 2012.
[c] Two-year average: Fall 2009–Fall 2011; Urban sites very low or zero precipitation in Summer 2010.

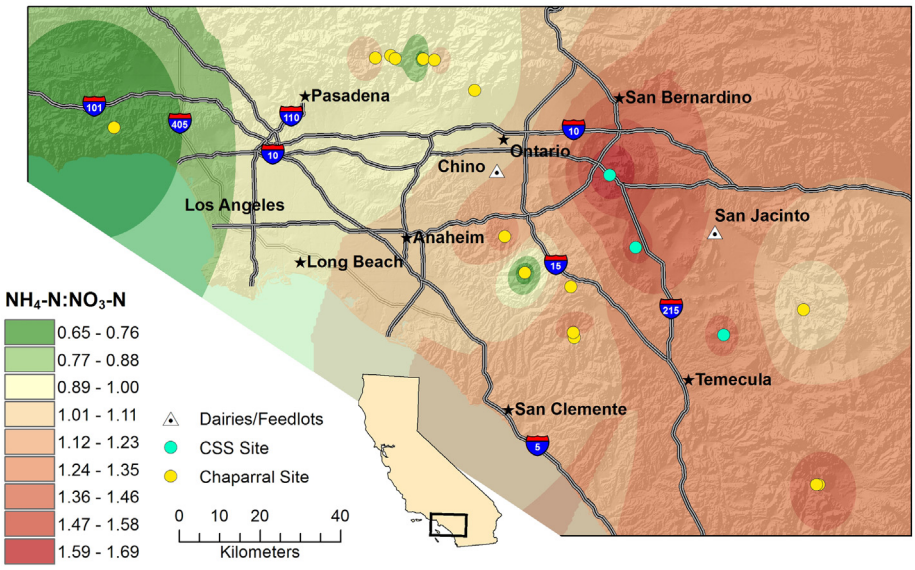


Fig. 7. Inverse distance weighting prediction map of ratios of NH_4-N:NO_3-N in annual throughfall deposition samples collected under chaparral and coastal sage scrub canopies in the Los Angeles Air Basin.

and by an NH_3 emissions source area from dairy farms in the Chino/Norco region approximately 60 km east of Los Angeles (115,000 cows in 2012; Kean et al., 2009, Leifer et al., 2017). Fraser and Cass (1998) reported that NH_3 emissions from light-duty motor vehicles equipped with three-way catalytic converters are similar in magnitude to agricultural emissions in the Los Angeles Air Basin. The effect of emissions from the dairies in the Basin can be seen in Fig. 5, in which the Camp Paivika site, located downwind from the dairies, has consistently higher NH_3 concentrations than Tanbark Flat, which is downwind of Los Angeles but upwind of the dairies. Likewise, the Santa Margarita site is too far south to be affected by the dairies and also has lower NH_3 concentrations than Camp Paivika. Leifer et al. (2017) reported elevated NH_3 along the south-facing slopes of the San Gabriel and San Bernardino Mountains and along the eastern Interstate 10 corridor extending eastward to Palm Springs. This result confirms the elevated NH_3 concentrations we report for Camp Paivika located on the SW end of the San Bernardino Mountains.

Sun et al. (2017) determined that CO_2-based estimates of NH_3 emissions from vehicles were twice that of the emissions reported in the 2011 NEI. They calculated that their emissions estimates increased on-road sources from 3% to 7% of the total U.S. NH_3 emissions inventory. We found similar differences between the NEI 2011 on-road NH_3 emissions data (3% of total) to CO_2-based estimates of NH_3 emissions for 2012 (8% of total NH_3 emissions). Sun et al. (2017) also estimated that vehicular NH_3 emissions are greater than agricultural emissions in counties containing nearly half of the U.S. population. Accounting for the seasonality of agricultural NH_3 emissions, with lower emissions in winter, Sun et al. (2017) estimated that on-road emissions account for as much as 13% of total national emissions in winter when particulate air pollution is often worse in urban areas.

4.2. Proportional deposition of NO_3-N and NH_4-N in urban and urban-affected areas

4.2.1. NADP/NTN wet deposition data

In the NADP national wet deposition network, deposition of NH_4-N increased at the urban influenced sites, but at a much slower rate than the agriculturally-affected NADP sites. Six of the eight urban-affected NADP sites switched from higher deposition of NO_3-N to equivalent or greater deposition of NH_4-N between 2005 and 2010. This switch resulted from a combination of decreasing NO_3^- deposition and slowly increasing NH_4^+ deposition. The rate of decline in NO_3^- wet deposition was similar at the predominantly agricultural (mean of 0.17 μeq L^{-1} yr^{-1}) and urban-affected (mean of 0.25 μeq L^{-1} yr^{-1}) NADP sites. The strong increases in NH_4^+ deposition at agricultural sites is presumably a result of continuing intensification of fertilizer use and large confined animal feeding operations. A similar but more muted increasing NH_4-N deposition trend was observed at CA75, a site in Sequoia National Park. This park site is not immediately adjacent to agricultural activities, but is exposed to the upwind extensive agricultural area of the Central Valley of California, as well as local traffic and on-road and urban emissions in the Central Valley. Thus, the rate of NH_4-N deposition at CA75 more closely parallels that of other NADP sites strongly affected by agricultural emissions.

In contrast to the agriculturally-affected sites, the increases in NH_4^+ deposition in urban-influenced NADP sites are likely attributable to two principal factors: (1) population increases and increased fuel consumption in the transportation sector, and (2) the increasing proportion of vehicular nitrogenous emissions as NH_3 (Bishop and Stedman, 2015). This is in large part because of NOx emissions control technologies on newer heavy duty vehicles, including city buses, refuse trucks and cargo vehicles, as well as light-duty diesel powered cars, that all produce NH_3 (Bishop and Stedman, 2015).

4.2.2. Bulk and throughfall deposition in urban-affected regions

The NH_4-N:NO_3-N ratios in wet and bulk deposition in the cities of Portland and Eugene, Oregon, and Seattle, Washington suggest higher deposition fluxes of NH_4-N than NO_3-N in these urban sites. Ion ratios in bulk deposition were highest at the Portland Zoo site (2.9), presumably because of additional NH_3 emissions from animal excrement. In bulk deposition at urban sites in the Los Angeles Basin, deposition of NH_4-N and NO_3-N were highly similar to each other, while ratios of NH_4-N:NO_3-N in throughfall under shrubs ranged from 0.7 to 1.5 across a network of chaparral and coastal sage scrub sites. These findings suggest that, in these urban areas, on-road and possibly other urban sources of NH_3 emissions, are leading to levels of NH_4-N deposition that are similar to or greater than NO_3-N deposition. Likewise at the NADP site immediately downwind of Portland (WA98) and within the Columbia River Gorge, 60% of wet inorganic N deposition is in the NH_4-N form compared to 54% at the Tanbark Flat site (CA42) just east of Los Angeles. The high levels of on-road emissions of NH_3 in these areas (Fig. 2a) suggests that the relatively high NH_4^+ deposition in these urban and urban-affected sites are primarily a result of vehicular NH_3 emissions. Likewise, in the Lake Tahoe Basin, the strong correlation between summertime

NH_3 concentrations and NH_4^+ in bulk deposition and throughfall—and the elevated NH_4-N:NO_3-N ratios in bulk deposition and throughfall (1.4 and 1.6, respectively), provide another example of the importance of tailpipe and possibly other urban sources of NH_3 as drivers of NH_4^+ deposition in urbanized regions. These relationships were particularly evident at the Valhalla site, nearest to the city of South Lake Tahoe. However, some evidence suggests that long-range transport of NH_3 from the San Joaquin Valley may also contribute to N deposition in the Tahoe Basin (Dolislager et al., 2012; Pearson et al., 2015).

The study of Rao et al. (2014) along a Boston to Harvard Forest urbanization gradient illustrates the principal tenet of our study–that near urban centers or road networks, on-road NH_3 emissions have a considerable effect on N deposition. Rao et al. (2014) report that closer to urban centers and high density road networks, throughfall N deposition under hardwoods, and in particular NH_4-N deposition, is higher than in rural sites. In urban sites 77% of the N deposition was as NH_4-N and was three times greater than NO_3-N deposition. However, the regional-scale deposition model used in their study (ClimCalc; Ollinger et al., 1993) did not discern this fine scale variation in deposition, and the model indicated that NO_3-N deposition was much higher than NH_4-N deposition, presumably because the model doesn't account for on-road emissions of NH_3. Similarly, Decina et al. (2017) reported that NH_4-N deposition comprised 75% of N deposition across the urban area of Boston, that NH_4-N deposition rates were correlated with NH_3 emissions and proximity to roads, and that NH_4-N deposition inputs were highest in spring. It was postulated that volatilization and re-deposition of fertilizer is the likely source of the springtime NH_4-N deposition spike (Decina et al., 2017).

4.3. NH_3 concentrations in urban-affected west coast regions

Trends of increasing proportions of atmospheric N as NH_3 and decreasing proportions as NO_y in the Los Angeles Basin sites support the long term wet deposition data from Tanbark Flat (NADP site CA42) showing increasing NH_4^+ and decreasing NO_3^- wet deposition. Roadway studies from the San Francisco peninsula in 2002 and 2010 demonstrate the general trend of increasing on-road emissions of NH_3 and decreasing on-road NO_x emissions. Although concentrations of NO_x were 5-fold greater than NH_3 in 2010, concentrations of NH_3 had increased nearly 5-fold from 2002. It was previously found that N deposition at the Edgewood sites is dominated by NH_4-N originating from on-road NH_3 emissions (Fenn et al., 2010). The disproportionately higher deposition of NH_4-N at Edgewood, despite the higher atmospheric concentrations of NO_x, is due to the higher reactivity and deposition velocity of NH_3 compared to NO and NO_2 (Zhang et al., 2012). It is not clear why NH_3 concentrations decreased at the Edgewood near site (50 m from road) from 2002 to 2010, but considering the Edgewood far site (530 m from road) and all five study sites, it seems clear that the more general pattern is one of increasing NH_3 concentrations near roadways, which highlights the increasing contribution of on-road NH_3 emissions to N deposition in urban areas and ecosystems located downwind.

4.4. Environmental and ecological implications of urban and on-road NH_3 emissions

Urbanized regions are hotspots of N emissions when viewed within the larger landscape. Urban emissions can cause harmful effects both within urban areas and also to downwind ecosystems as a result of exposure to ozone, N compounds and S deposition. A recent analysis of 14 metropolitan areas in the U.S. concluded that 60–80% of the impacts of urban emissions occur outside of the urban zone (Heo et al., 2017). Emissions reductions of SO_2 and NO_x have caused deposition of SO_4^{2-} and NO_3^- to decline considerably across most of the U.S. (Vet et al., 2014), even in remote mountain regions (Heard et al., 2014), while increased production of NH_3 from agriculture and vehicles has caused an increase in chemically-reduced forms of N deposition (Thiruvengadam et al., 2016).

Moreover, while the effects of N deposition on aquatic and terrestrial ecosystems are well known, these broad patterns are complicated by growing evidence that reduced forms of N cause more severe ecosystem responses than oxidized N forms (Dias et al., 2014; Glibert, 2010; Kleijn et al., 2008; Mur et al., 2017; Stevens et al., 2011; Van den Berg et al., 2005, 2016; Verhoeven et al., 2011). These differential effects depending on N form may grow in importance as the proportion of N deposition in reduced forms continues to increase.

Although total agricultural NH_3 emissions in CONUS dwarf those in urban areas, 40% of the US population lives within counties where on-road emissions are greater than agricultural NH_3 emissions, which attests to the importance of urban and on-road emissions. On-road emissions of NH_3 are thus of great importance for human health due to the key role that NH_3 plays in the formation of particulate air pollution (Schiferl et al., 2014). Air pollution is also an important issue for the many local, state and national parks and other public and private recreational areas that are in regions where air quality, regional haze, visibility impairment and N deposition impacts are strongly affected by urban and on-road emissions. Particulate forms of N also allow for long-range transport of atmospheric N, thus contributing to N deposition effects in wildland areas located downwind of emission sources (Heard et al., 2014; Hertel et al., 2013).

In a study from a watershed in Cape Cod, Massachusetts, Bettez et al. (2013) found increased N deposition near roads mainly due to NH_4^+ deposition from mobile source emissions. Not accounting for these near-source N emissions resulted in underestimates of N deposition for the watershed of 13–25%. The authors concluded that in arid or semiarid sites, where fog deposition is important, or in areas near roads, regional monitoring networks underestimate N deposition. Likewise, as suggested by data in the present study, on-road NH_3 emissions are a dominant source of NH_4^+ deposition in the Lake Tahoe Basin and in the Los Angeles, San Francisco, San Jose and other West Coast metropolitan areas and surrounding regions. The significance of on-road and urban emissions of NH_3 has been demonstrated in many regions (Cape et al., 2004; Decina et al., 2017; Gadsdon and Power, 2009; Kirchner et al., 2005; Rao et al., 2014; Watmough et al., 2014). However, some studies of on-road N emissions have measured oxidized forms of N, while ignoring NH_3 emissions (Gombert et al., 2003; Kenkel et al., 2016), possibly because on-road emissions are as of yet, sometimes underappreciated.

5. Conclusions

Emissions inventories and trends in atmospheric NH_3 concentrations are uncertain, largely because NH_3 is not a USEPA criteria pollutant, and thus data are lacking. Our estimates of on-road emissions of NH_3 within CONUS (0.26 Tg yr^{-1}) are 2.9 times greater than those of the USEPA's NEI (0.09 Tg yr^{-1}). Empirical monitoring data indicate the increasing importance of reduced forms of atmospheric N in the environment. Ammonium constitutes 58.7% of wet inorganic N deposition at sites within CONUS. Only 4% of the NADP stations had <45% of the N deposition as NH_4^+ based on data from 2014 to 2016, illustrating the near-universal occurrence of relatively high NH_4^+ deposition across the United States. Although agricultural emissions in CONUS are 11-fold greater than emissions from the transport sector, we identified 440 counties where at least one-third of the NH_3 emissions are from on-road sources. Ratios of NH_4-N:NO_3-N in wet, bulk and throughfall deposition data in urban and near-urban sites indicate the importance of on-road and urban emissions of NH_3 in the N deposition budgets of these regions.

As a result of expanding urbanization worldwide and the increasing segments of the transportation sector that emit NH_3, on-road emissions of NH_3 are becoming greater contributors to atmospheric NH_3, particulate pollution formation (e.g., $PM_{2.5}$) and elevated N deposition. This has major implications for human and ecosystem health, visibility and

climate change. These harmful impacts are observed in urban, suburban, rural and natural areas. Reduced forms of N can be particularly harmful to some ecosystems and vegetation types, and increased levels of particulate air pollution are a major aesthetic detriment in recreation areas as well as a threat to the well-being of recreationists. The relative contribution of NH_3 emissions from agricultural versus urban or on-road sources varies across the landscape, but both are important N emissions sources in many regions, although urban and on-road emissions of NH_3 are often underappreciated.

References

Battye, W., Aneja, V.P., Schlesinger, W.H., 2017. Is nitrogen the next carbon? Earth's Future 5 11 p. https://doi.org/10.1002/2017EF000592.

Bettez, N.D., Marino, R., Howarth, R.W., Davidson, E.A., 2013. Roads as nitrogen deposition hot spots. Biogeochemistry 114, 149–163.

Bishop, G.A., Stedman, D.H., 2015. Reactive nitrogen species emission trends in three light-/medium-duty United States fleets. Environ. Sci. Technol. 49, 11234–11240.

Bytnerowicz, A., Sanz, M.J., Arbaugh, M.J., Padgett, P.E., Jones, D.P., Davila, A., 2005. Passive sampler for monitoring ambient nitric acid (HNO_3) and nitrous acid (HNO_2) concentrations. Atmos. Environ. 39, 2655–2660.

Bytnerowicz, A., Fenn, M., Allen, E.B., Cisneros, R., 2016. Atmospheric Chemistry. In: Mooney, H., Zavaleta, E. (Eds.), Ecosystems of California. University of California Press, Oakland, California, pp. 107–128 (984 p).

Cape, J.N., Tang, Y.S., van Dijk, N., Love, L., Sutton, M.A., Palmer, S.C.F., 2004. Concentrations of ammonia and nitrogen dioxide at roadside verges, and their contribution to nitrogen deposition. Environ. Pollut. 132, 469–478.

DARTE, 2017. Carbon Monitoring System (CMS): Database of Road Transportation Emissions (DARTE) Annual On-road CO_2 Emissions on a 1-km Grid. Conterminous USA: pp. 1980–2012. https://daac.ornl.gov/CMS/guides/CMS_CO2_Relationships.html.

Decina, S.M., Templer, P.H., Hutyra, L.R., Gately, C.K., Rao, P., 2017. Variability, drivers, and effects of atmospheric nitrogen inputs across an urban area: emerging patterns among human activities, the atmosphere, and soils. Sci. Total Environ. 609, 1524–1534.

Dias, T., Clemente, A., Martins-Louēćo, M.A., Sheppard, L., Bobbink, R., Cruz, C., 2014. Ammonium as a driving force of plant diversity and ecosystem functioning: observations based on 5 years' manipulation of N dose and form in a Mediterranean ecosystem. PLoS One 9 (4), e92517.

Dolislager, L.J., VanCuren, R., Pederson, J.R., Lashgari, A., McCauley, E., 2012. A summary of the Lake Tahoe Atmospheric Deposition Study (LTADS). Atmos. Environ. 46, 618–630.

Du, E.Z., De Vries, W., Galloway, J.N., Hu, X.Y., Fang, J.Y., 2014. Changes in wet nitrogen deposition in the United States between 1985 and 2012. Environ. Res. Lett. 9, 95004 (8 pp).

Fenn, M.E., Poth, M.A., 2004. Monitoring nitrogen deposition in throughfall using ion exchange resin columns: a field test in the San Bernardino Mountains. J. Environ. Qual. 33, 2007–2014.

Fenn, M.E., Sickman, J.O., Bytnerowicz, A., Clow, D.W., Molotch, N.P., Pleim, J.E., Tonnesen, G.S., Weathers, K.C., Padgett, P.E., Campbell, D.H., 2009. Methods for measuring atmospheric nitrogen deposition inputs in arid and montane ecosystems of western North America. In: Legge, A.H. (Ed.), Developments in Environmental Science. Air quality and ecological impacts: relating sources to effects Vol. 9. Elsevier, Amsterdam, pp. 179–228.

Fenn, M.E., Allen, E.B., Weiss, S.B., Jovan, S., Geiser, L., Tonnesen, G.S., Johnson, R.F., Rao, L.E., Gimeno, B.S., Yuan, F., Meixner, T., Bytnerowicz, A., 2010. Nitrogen critical loads and management alternatives for N-impacted ecosystems in California. J. Environ. Manag. 91, 2404–2423.

Fraser, M.P., Cass, G.R., 1998. Detection of excess ammonia emissions from in-use vehicles and the implications for fine particle control. Environ. Sci. Technol. 32, 1053–1057.

Gadsdon, S.R., Power, S.A., 2009. Quantifying local traffic contributions to NO_2 and NH_3 concentrations in natural habitats. Environ. Pollut. 10, 2845–2852.

Gately, C.K., Hutyra, L.R., Wing, I.S., 2015. Cities, traffic, and CO_2: a multidecadal assessment of trends, drivers, and scaling relationships. Proc. Natl. Acad. Sci. 112, 4999–5004.

Glibert, P.M., 2010. Long-term changes in nutrient loading and stoichiometry and their relationships with changes in the food web and dominant pelagic fish species in the San Francisco estuary, California. Rev. Fish. Sci. 18, 211–232.

Gombert, S., Asta, J., Seaward, M.R.D., 2003. Correlation between the nitrogen concentration of two epiphytic lichens and the traffic density in an urban area. Environ. Pollut. 123, 281–290.

Heard, A.M., Sickman, J.O., Rose, N.L., Bennett, D.M., Lucero, D.M., Melack, J.M., Curtis, J.H., 2014. Twentieth-century atmospheric deposition and acidification trends in lakes of the Sierra Nevada, California (USA). Environ. Sci. Technol. 48, 10054–10061.

Heeb, N.V., Forss, A.M., Bruhlmann, S., Luscher, R., Saxer, C.J., Hug, P., 2006. Three-way catalyst-induced formation of ammonia—velocity- and acceleration-dependent emission factors. Atmos. Environ. 40, 5986–5997.

Heo, J., Adams, P.J., Gao, H.O., 2017. Public health costs accounting of inorganic $PM_{2.5}$ pollution in metropolitan areas of the United States using a risk-based source-receptor model. Environ. Int. 106, 119–126.

Hertel, O., Reis, S., Skjøth, C.A., Bleeker, A., Harrison, R., et al., 2011. Nitrogen processes in the atmosphere. In: Sutton, M.A., et al. (Eds.), The European Nitrogen Assessment. Cambridge University Press, Cambridge, pp. 177–207.

Hertel, O., Geels, C., Frohn, L.M., Ellermann, T., Skjøth, C.A., Løfstrøm, P., Christensen, J.H., Andersen, H.V., Peel, R.G., 2013. Assessing atmospheric nitrogen deposition to natural and semi-natural ecosystems - experience from Danish studies using the DAMOS. Atmos. Environ. 66, 151–160.

Homer, C.G., Dewitz, J.A., Yang, L., Jin, S., Danielson, P., et al., 2015. Completion of the 2011 National Land Cover Database for the conterminous United States-representing a decade of land cover change information. Photogramm. Eng. Remote. Sens. 81, 345–354.

Hůnová, I., Kurfürst, P., Stráník, V., Modlík, M., 2017. Nitrogen deposition to forest ecosystems with focus on its different forms. Sci. Total Environ. 575, 791–798.

Kean, A.J., Littlejohn, D., Ban-Weiss, G.A., Harley, R.A., Kirchstetter, T.W., Lunden, M.M., 2009. Trends in on-road vehicle emissions of ammonia. Atmos. Environ. 43, 1565–1570.

Kenkel, J.A., Sisk, T.D., Hultine, K.R., Sesnie, S.E., Bowker, M.A., Johnson, N.C., 2016. Indicators of vehicular emission inputs into semi-arid roadside ecosystems. J. Arid Environ. 134, 150–159.

Kirchner, M., Jakobi, G., Feicht, E., Bernhardt, M., Fischer, A., 2005. Elevated NH_3 and NO_2 air concentrations and nitrogen deposition rates in the vicinity of a highway in Southern Bavaria. Atmos. Environ. 39, 4531–4542.

Kleijn, D., Bekker, R.M., Bobbink, R., de Graaf, M.C.C., Roelofs, J.G.M., 2008. In search for key biogeochemical factors affecting plant species persistence in heathlands and acidic grasslands: a comparison of common and rare species. J. Appl. Ecol. 45, 680–687.

Leifer, I., Melton, C., Tratt, D.M., Buckland, K.N., Clarisse, L., et al., 2017. Remote sensing and *in situ* measurements of methane and ammonia emissions from a megacity dairy complex: Chino, CA. Environ. Pollut. 221, 37–51.

Leip, A., Achermann, B., Billen, G., Bleeker, A., Bouwman, A.F., et al., 2011. Integrating Nitrogen Fluxes at the European Scale. In: Sutton, M.A., et al. (Eds.), The European Nitrogen Assessment. Cambridge University Press, Cambridge, pp. 345–376.

Li, Y., Schichtel, B.A., Walker, J.T., Schwede, D.B., Chen, X., Lehmann, C.M.B., Puchalski, M.A., Gay, D.A., Collett Jr., J.L., 2016. Increasing importance of deposition of reduced nitrogen in the United States. Proc. Natl. Acad. Sci. 113, 5874–5879.

Li, Z., Jiang, J.K., Ma, Z.Z., Fajardo, O.A., Deng, J.G., Duan, L., 2017. Influence of flue gas desulfurization (FGD) installations on emission characteristics of $PM_{2.5}$ from coal-fired power plants equipped with selective catalytic reduction (SCR). Environ. Pollut. 230, 655–662.

Livingston, C., Rieger, P., Winer, A., 2009. Ammonia emissions from a representative in-use fleet of light and medium-duty vehicles in the California South Coast Air Basin. Atmos. Environ. 43, 3326–3333.

Moldanová, J., Grennfelt, P., Jonsson, A., Simpson, D., Springer, T., et al., 2011. Nitrogen as a threat to European air quality. In: Sutton, M.A., et al. (Eds.), The European Nitrogen Assessment. Cambridge University Press, Cambridge, pp. 405–433.

Mur, L.A.J., Simpson, C., Kumari, A., Gupta, A.K., Gupta, K.J., 2017. Moving nitrogen to the centre of plant defence against pathogens. Ann. Bot. 119, 703–709.

Ogawa & Company, USA, Inc., 2006. NO, NO_2, NOx and SO_2 sampling protocol using the Ogawa Sampler. 6th ed. Pompano Beach, FL. 30 p. http://ogawausa.com/wp-content/uploads/2014/04/prono-noxno2so206.pdf (14 November 2016).

Ollinger, S.V., Aber, J.D., Lovett, G.M., Millham, S.E., Lathrop, R.G., Ellis, J.M., 1993. A spatial model of atmospheric deposition for the Northeastern U.S. Ecol. Appl. 3, 459–472.

Pearson, C., Schumer, R., Trustman, B.D., Rittger, K., Johnson, D.W., Obrist, D., 2015. Nutrient and mercury deposition and storage in an alpine snowpack of the Sierra Nevada, USA. Biogeosciences 12, 3665–3680.

Pye, H.O.T., Liao, H., Wu, S., Mickley, L.J., Jacob, D.J., Henze, D.K., Seinfeld, J.H., 2009. Effect of changes in climate and emissions on future sulfate-nitrate-ammonium aerosol levels in the United States. J. Geophys. Res. 114, D01205. https://doi.org/10.1029/2008JD010701.

Rao, P., Hutyra, L.R., Raciti, S.M., Templer, P.H., 2014. Atmospheric nitrogen inputs and losses along an urbanization gradient from Boston to Harvard Forest, MA. Biogeochemistry 121, 229–245.

Roadman, M.J., Scudlark, J.R., Meisinger, J.J., Ullman, W.J., 2003. Validation of Ogawa passive samplers for the determinations of gaseous ammonia concentrations in agricultural settings. Atmos. Environ. 37, 2317–2325.

Schiferl, L.D., Heald, C.L., Nowak, J.B., Holloway, J.S., Neuman, J.A., et al., 2014. An investigation of ammonia and inorganic particulate matter in California during the CalNex campaign. J. Geophys. Res. Atmos. 119, 1883–1902.

Stevens, C.J., Manning, P., Van Den Berg, L.J.L., De Graaf, M.C.C., 2011. Ecosystem responses to reduced and oxidised nitrogen inputs in European terrestrial habitats. Environ. Pollut. 159, 665–676.

Sun, K., Tao, L., Miller, D.J., Pan, D., Golston, L.M., et al., 2017. Vehicle emissions as an important urban ammonia source in the United States and China. Environ. Sci. Technol. 51, 2472–2481.

Thiruvengadam, A., Besch, M., Carder, D., Oshinuga, A., Pasek, R., Hogo, H., Gautam, M., 2016. Unregulated greenhouse gas and ammonia emissions from current technology heavy-duty vehicles. J. Air Waste Manage. Assoc. 66, 1045–1060.

U.S. Census Bureau, 2017. TIGER/Line Shapefiles (machine-readable data files). Spatial Data Collection and Products Branch Geography Division. U.S. Census Bureau 4600 Silver Hill Road, Washington, DC, p. 20233-7400 (Accessed April, 2017).

USEPA, 2017. Air emissions inventories. 2014 National Emissions Inventory (NEI) Data. United States Environmental Protection Agency (Accessed April 2017). https://www.epa.gov/air-emissions-inventories/2014-national-emissions-inventory-nei-data.

Vallero, D., 2014. Fundamentals of Air Pollution. 5th Ed. Academic Press, Boston, Massachusetts, USA (986 pp).

Van den Berg, L.J.L., Dorland, E., Vergeer, P., Hart, M.A.C., Bobbink, R., Roelofs, J.G.M., 2005. Decline of acid-sensitive plant species in heathland can be attributed to ammonium toxicity in combination with low pH. New Phytol. 166, 551–564.

Van den Berg, L.J.L., Jones, L., Sheppard, L.J., Smart, S.M., Bobbink, R., Dise, N.B., Ashmore, M.R., 2016. Evidence for differential effects of reduced and oxidised nitrogen deposition on vegetation independent of nitrogen load. Environ. Pollut. 208, 890–897.

Verhoeven, J.T.A., Beltman, B., Dorland, E., Robat, S.A., Bobbink, R., 2011. Differential effects of ammonium and nitrate deposition on fen phanerogams and bryophytes. Appl. Veg. Sci. 14, 149–157.

Vet, R., Artz, R.S., Carou, S., Shaw, M., et al., 2014. A global assessment of precipitation chemistry and deposition of sulfur, nitrogen, sea salt, base cations, organic acids, acidity and pH, and phosphorus. Atmos. Environ. 93, 3–100.

Watmough, S.A., McDonough, A.M., Raney, S.M., 2014. Characterizing the influence of highways on springtime NO_2 and NH_3 concentrations in regional forest monitoring plots. Environ. Pollut. 190, 150–158.

Xing, J., Pleim, J., Mathur, R., Pouliot, G., Hogrefe, C., Gan, C.-M., Wei, C., 2013. Historical gaseous and primary aerosol emissions in the United States from 1990 to 2010. Atmos. Chem. Phys. 13, 7531–7549.

Zhang, L., Vet, R., O'Brien, J.M., Mihele, C., Liang, Z., Wiebe, A., 2009. Dry deposition of individual nitrogen species at eight Canadian rural sites. J. Geophys. Res. 114, D02301 13 pp.

Zhang, L., Jacob, D.J., Knipping, E.M., Kumar, N., Munger, J.W., et al., 2012. Nitrogen deposition to the United States: distribution, sources, and processes. Atmos. Chem. Phys. 12, 4539–4554.