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# Increasing ammonia concentration trends in large regions of the USA derived from the NADP/AMoN network

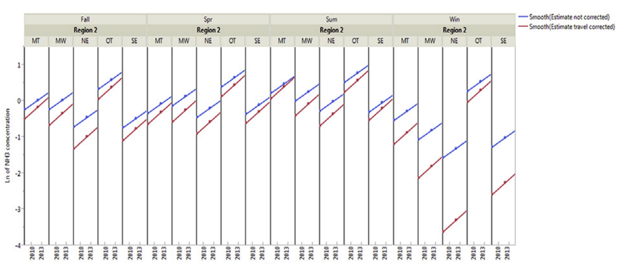
T. Butler [a, b, *], F. Vermeylen [c], C.M. Lehmann [d], G.E. Likens [b, e], M. Puchalski [f]

[a] Cornell University, Dept. of Ecology and Evolutionary Biology, Ithaca, NY 14853, USA
[b] Cary Institute of Ecosystem Studies, Box AB, Millbrook, NY 12545, USA
[c] Cornell University Office of Statistical Consulting, Ithaca, NY 14853, USA
[d] NADP Program Office, Illinois State Water Survey, Champaign, IL 61820, USA
[e] Dept. of Ecology and Evolutionary Biology, University of Connecticut, Storrs, CT 06269, USA
[f] U.S. EPA Office of Air Programs, Washington D.C. 20460, USA

## HIGHLIGHTS

- Emissions of $NH_3$ are assessed to be nearly constant in the USA from 2008 to 2014.
- $NH_3$ air concentrations and precipitation $NH_4^+$ show increasing trends over a large area of the USA from 2008 to 2015.
- Particulate $NH_4^+$, $NO_3^-$ and $SO_4^{2-}$ show decreasing trends in these regions.
- Declining NOx and $SO_2$ emissions provide less $H_2SO_4$ and $HNO_3$ for neutralization of $NH_3$ in the atmosphere.
- Greater $NH_3$ concentrations may change the spatial pattern of N deposition.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Data from bi-weekly passive samplers from 18 of the longest operating National Atmospheric Deposition Program's (NADP) Ammonia Monitoring Network (AMoN) sites (most operating from 2008 to 2015) show that concentrations of $NH_3$ have been increasing ($p$-value $< 0.0001$) over large regions of the USA. This trend is occurring at a seasonal and annual level of aggregation. Using random coefficient models (RCM), the mean slope for the 18 sites combined shows an increase of $NH_3$ concentration of +7% per year, with a 95% confidence interval (C.I.) from +5% to +9% per year. Travel blank corrected data using the same approach show increasing $NH_3$ concentrations of +9% (95% C.I. +5% to +13%) per year. During a comparable period (2008–2014) NADP precipitation chemistry sites in the same regions show significant increasing ($p$-value $= 0.0001$) precipitation $NH_4^+$ concentrations trends for all sites combined of +5% (95% C.I. +3% to +7%) per year.

Emissions inventory data for the study period show nearly constant rates of $NH_3$ emissions, but large reductions in NOx and $SO_2$ emissions. Seasonal air quality data from the Clean Air Status and Trends Network (CASTNET) sites in these regions show significant declines in atmospheric particulate $SO_4^{2-}$ and $NH_4^+$, and particulate $NO_3^-$ plus $HNO_3$ (total $NO_3^-$) during the same period. Less formation of acidic $SO_4$ and $NO_3$, due to reduced $SO_2$ and NOx emissions, provide less substrate to interact with $NH_3$ and form particulate ammonium species. Thus, concentrations of $NH_3$ can increase in the atmosphere even if

* Corresponding author. 211 Rice Hall, Cornell University, Ithaca, NY 14853, USA.
*E-mail address:* tjb2@cornell.edu (T. Butler).

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emissions remain constant. A likely result may be more localized deposition of $NH_3$, as opposed to the more long-range transport and deposition of ammonium nitrate ($NH_4NO_3$) and sulfate $(NH_4)_2SO_4$). Additionally, the spatial distribution of wet and dry acidic deposition will be impacted.



## 1. Introduction

Anthropogenic nitrogen oxides (nitrogen oxide (NO) + nitrogen dioxide ($NO_2$) = NOx) emissions have been in decline in the USA since ~2001, but this has not been the case for ammonia ($NH_3$) (EPA, 2015a; NEI, 2015). National data from the EPA National Emissions Inventory (NEI) show that NOx and $NH_3$ emissions, expressed as million metric tons (or taragrams) of N, are now approximately the same magnitude (Fig. 1). Programs such as the NOx Budget Trading Program, implemented in 2003, and the Clean Air Interstate Rule, implemented in 2009, have led to a 66% reduction, between 2000 and 2013, in stationary (i.e. electric generating units and industrial boilers) NOx emissions (EPA, 2015b). USA national $NH_3$ emissions, have shown a minor increase until 2008, and since then emissions have remained relatively constant, according to the NEI inventory (NEI, 2015).

It is estimated that over 80% of $NH_3$ emissions are from anthropogenic sources (Behera et al., 2013). In the USA over 80% of these $NH_3$ emissions are from agriculture (EPRI, 2015), with 54% derived from livestock production and 30% from volatilization of nitrogen based fertilizer (Xing et al., 2013). However, because $NH_3$ is not considered a criteria pollutant and therefore is not regulated at the federal level, these data can have a higher degree of uncertainty (Reis et al., 2009; EPRI, 2015) than more regulated emissions such as NOx and $SO_2$. The $NH_3$ emissions data are somewhat limited and rely on states reporting emission data for non-stationary sources (i.e. agricultural practices), as well as data from local and tribal air resource agencies (NEI, 2015). Comprehensive $NH_3$ emission inventories are done only every three years (e.g. 2008 and 2011, with 2014 not completed), and many smaller $NH_3$ sources are not required to be reported. Other localized impacts include changes in fertilizer type, means of application and rotation of crops (Paulot et al., 2014). Short term localized weather patterns may also impact fertilizer and manure volatilization and $NH_3$ emission rates, but such changes are likely unreported. All of these factors can add to the uncertainty in $NH_3$ emission rates.

State-level data for the years 2008 and 2011 are available (Fig. 2). Based on this limited data set it appears that changes in state $NH_3$ emissions are also small in the states where "long-term" National Atmospheric Deposition Program (NADP)/Ammonia Monitoring Network (AMoN) $NH_3$ monitoring sites used in this study are located. Another state level emissions data set (EPRI, 2015) from the Electric Power Research Institute (EPRI) substantiates the NEI emission estimates, and is included in Fig. 2. Additionally, Xing et al. (2013) separately quantify emissions in the USA for the period 1990 to 2010. Their inventory shows a lower estimate of $NH_3$ emissions than the NEI, but after 2002 the lack of a trend is consistent with the NEI lack of trend.

Ammonia is the most abundant alkaline gas in the atmosphere and can directly deposit to the ecosystem, or neutralize acidic components and form particulate matter which can degrade visibility. (Behera et al., 2013). In addition ammonia and ammonium species impact nitrogen sensitive landscapes. At the Acid Rain Conference 2015 meeting in Rochester, NY (Acid Rain, 2015) a number of speakers concluded that both in North America and Europe, $NH_3$ emissions need to be reduced, when reducing total nitrogen deposition to sensitive ecosystems is a concern. The development of a national $NH_3$ monitoring network, that began in the fall of 2007, allows the determination of whether any regional and/or temporal changes in the ground-level $NH_3$ concentrations have occurred, and if the lack of change in $NH_3$ emissions is reflected in seasonal and annual AMoN concentrations. An eight year record is by many standards not very "long-term" (Lindenmayer and Likens, 2010), but the NADP/AMoN represents the longest operating $NH_3$ network in the USA, with consistent well documented protocols and analysis procedures (NADP, 2014a; 2014b). We present our findings based on the 18 sites with the longest operation in the network.

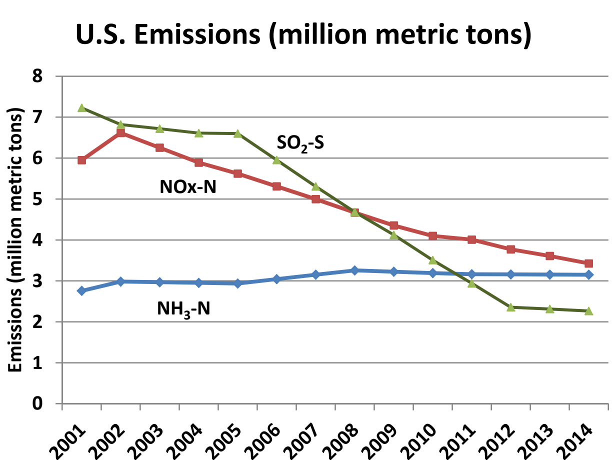


**Fig. 1.** National Emission Inventory (NEI, 2015) $SO_2$ (reported as S), NOx and $NH_3$ (both reported as N) emissions from 2001 to 2014. NOx is assumed to be in the form of $NO_2$.

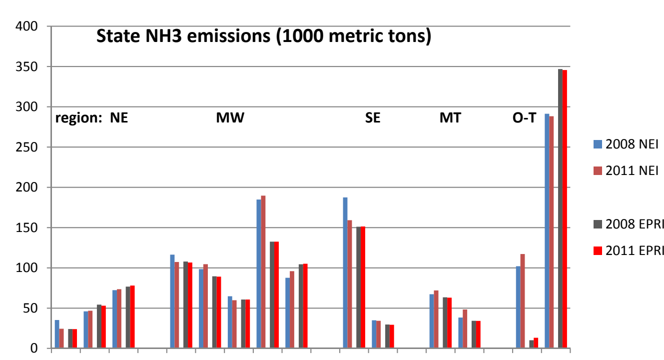


**Fig. 2.** Selected state-level $NH_3$ emissions for 2008 and 2011. There are two sources of emissions data, the NEI (first 2 bars) and a separate accounting done by EPRI (last 2 bars for each state) (EPRI, 2015). Regions are: MT = mountain, MW = midwest, NE = northeast, OT = Oklahoma – Texas, SE = southeast.