Improved reduced nitrogen deposition estimates in the United States: Spatial variability of ammonia

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Abstract
The Clean Air Status and Trends Network (CASTNET) is the only long-term monitoring network in the United States that provides estimates of dry deposition for sulfur and nitrogen species. CASTNET measures ambient concentrations that are combined with modeled deposition velocities to estimate dry deposition at more than 90 sites. Until recently, concentrations of NH_3 were not routinely measured at CASTNET sites, resulting in a significant gap in the total nitrogen budget. Between 2008 and 2015, more than 60 National Atmospheric Deposition Program (NADP) Ammonia Monitoring Network (AMoN) sites were deployed at CASTNET sites, providing ambient NH_3 concentrations.

Estimates of total (wet + dry) deposition are provided by combining measured ambient concentrations and wet deposition fluxes with modeled estimates of dry deposition velocities and fluxes for unmeasured species (Schwede and Lear, 2015). The NADP's total deposition (TDEP) hybrid method combines data from several routine monitoring networks and the Community Multi-scale Air Quality (CMAQ) model. The deposition fluxes are interpolated to create a continuous surface using inverse distance weighting (Figure 1). NH_3 may not be well characterized in the model and influences from emissions sources may impact the radius of influence between sites. This paper describes results from an NH_3 spatial variability study designed to improve the spatial interpolation methods used in the TDEP maps. During this study, supplemental passive NH_3 monitoring sites were randomly distributed around the Bondville, IL (IL11) and Fort Collins, CO (CO13) AMoN sites for one year. Results from this analysis will improve future gridded total deposition estimates.

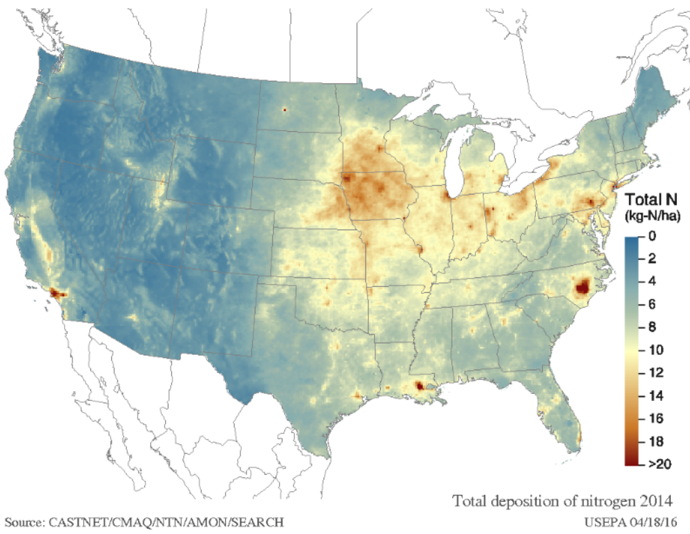

Figure 1. Total nitrogen deposition (2014) from TDEP map version 2016.01.

Key Words
Ammonia, deposition, CASTNET, spatial variability, long-term monitoring, reduced nitrogen

Introduction
Reduced nitrogen measurements have been made in the form of NH_4^+ concentrations and NH_4^+ in precipitation by CASTNET (www.epa.gov/castnet) and NADP's National Trends Network (NTN)

(www.nadp.isws.illinois.edu/ntn) for more than 25 years. Network-wide measurements of ambient NH_3 were not available until 2007 when NADP adopted AMoN (www.nadp.isws.illinois.edu/amon). AMoN now provides bi-weekly measurements of gaseous NH_3 at more than 90 sites throughout the contiguous US, Alaska, Canada and Puerto Rico.

Difficulties in estimating total deposition were addressed by the Total Deposition Science Committee in 2014. Hybrid maps were developed using measurement data from NADP's wet deposition networks, CASTNET, AMoN, and the Southeastern Aerosol Research and Characterization (SEARCH) network and modeled data from CMAQ. In 2016, AMoN was excluded from the TDEP maps because a bi-directional NH_3 flux model was added to CMAQ which doesn't allow for calculated fluxes using bi-weekly concentrations. Work is underway to develop a model suitable for estimating bi-directional fluxes of NH_3 using measured AMoN concentrations. The work of Li et. al. (2016) represents the first step of this development. Here we evaluate the spatial variability between AMoN sites to identify a radius of influence for use in TDEP or other NH_3 concentration gradient map products. The spatial variability of NH_3 has been studied within or near emissions sources, but has not been verified on a regional scale (i.e. Dragosits et. al., 2002; Walker et. al., 2004). Pinder et. al. (2011) studied NH_3 in a region of mixed crop and animal production in the southeastern U.S. using satellite retrievals, confirming the large spatial variability observed with ground-based point measurements.

Methods

AMoN Sampling

The NADP's AMoN sites utilize Radiello© passive samplers to measure bi-weekly concentrations of gaseous NH_3. Samplers are prepared, shipped, and analyzed at the Illinois State Water Survey/Central Analytical Laboratory. Exposed samplers are analyzed for NH_4^+ by Flow Injection Analysis (Lachat Analytics, Inc., QuikChem 8500 Series II, Milwaukee, WI). Background information about the AMoN methods can be found in Puchalski et. al. (2011).

The locations of the Bondville (IL11) and Fort Collins (CO13) supplemental sites are shown in Figure 2. There were nine supplemental sites deployed around the IL11 AMoN site beginning in December 2014. The IL11 and surrounding supplemental sites are influenced by agriculture (crop production, fertilizer applications). Samplers were shipped to each supplemental site on a 1:6 sample schedule for at least one year. Precision was calculated based on triplicate samplers being deployed during approximately 25% of the sample periods in each region. Travel blanks were shipped during approximately 10% of the sample periods. Travel blanks were not removed from the glass shipping containers and were returned to the lab with the corresponding ambient sample.

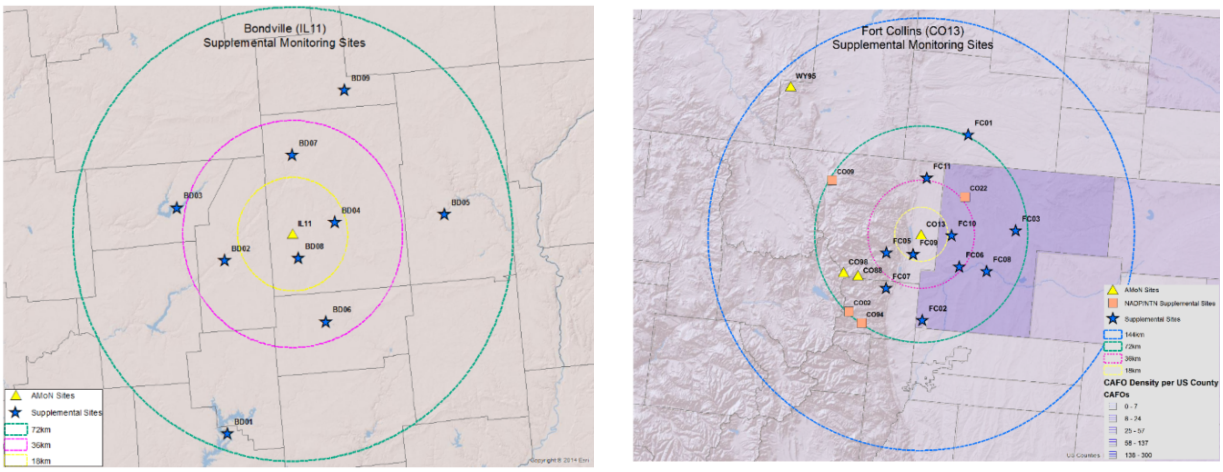

Figure 2. Spatial distribution of supplemental AMoN sites around (a) Bondville IL (IL11) and (b) Fort Collins CO (CO13) AMoN sites. Circles represent 18, 36, 72 and 144 km radial distances around the AMoN sites.

Model

CMAQ is a regional air quality model that utilizes year specific meteorology, emissions from mobile and stationary sources, and land use classifications to predict atmospheric concentrations and deposition in the

US (Byun and Schere, 2006). CMAQ version 5.02 was used to create 12km grids of unmeasured species combined with monitoring data from 2000-2014 to produce the 2016v01 TDEP maps (Figure 1).

The interpolation distance used in the inverse distance weighting varies by pollutant and season (Schwede and Lear 2014). Schwede and Lear (2014) used CMAQ modeled gridded data to create normalized covariance plots for each pollutant. Distances corresponding to a covariance of 0.7 were selected for each pollutant for each season for the inverse distance weighting. Measured concentrations of NH_3 were not included in TDEP version 2016.01 because of the inclusion of the bi-directional flux model in CMAQ. Current information about the TDEP method and results can be found on the Total Deposition Science Committee webpage (www.nadp.isws.illinois.edu/committees/tdep). The maximum distance of influence for NH_3 was verified using measured data from more than 20 supplemental NH_3 monitoring sites over a year. Supplemental sites were placed around two existing AMoN sites, Bondville, IL (IL11) and Fort Collins, CO (CO13). The AMoN sites are impacted by crops/fertilizer application and animal operations, respectively, and vary significantly in terrain and land use.

In subsequent versions of TDEP, the measured NH_3 concentrations should be included in the bi-directional framework. Work is underway to utilize the bi-weekly AMoN concentrations in the flux model. Modeled bi-directional fluxes will be calculated during a site characterization pilot study in 2017. During the pilot, inputs to the bi-directional flux model including soil and vegetation chemistry, meteorology, and canopy characteristics will be collected. Results from the pilot will then be used to build a box model for estimating positive or negative fluxes from the bi-weekly concentrations at all AMoN sites. Results from the spatial variability study and the site characterization pilot will provide the TDEP community with improved estimates of NH_3 for the next version of the TDEP maps.

Results

A statistical analysis was performed to calculate a reasonable radius of influence of NH_3 for performing the inverse distance weighting. A linear regression was plotted for each site pair (n=45 for Bondville, IL) to determine the correlation between each pair (r^2). The correlation was plotted against the distance between the site pairs to determine the distance at which the variability between sites is no longer explained. The Bondville and Fort Collins results are shown in Figure 3 below. The median r^2 for the Bondville data is 0.9. From this analysis we assume we can explain the variability between sites up to a distance of 115km.

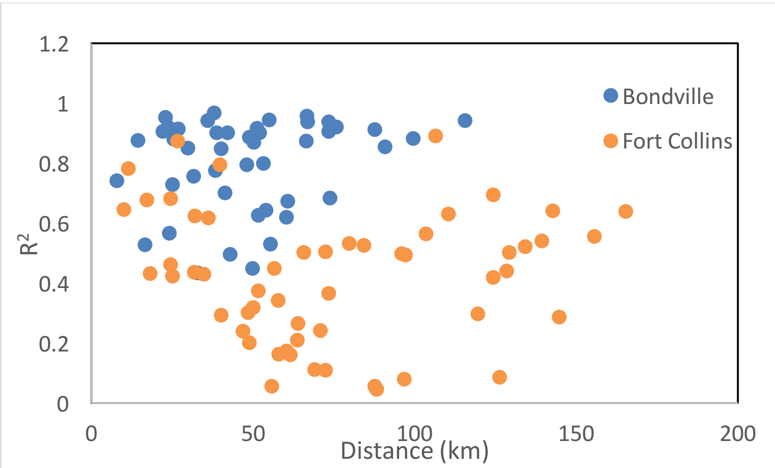

Figure 3. Site pair correlations versus distance between site pairs for Bondville and Fort Collins. Fort Collins data excludes the Weld County data which is heavily influenced by CAFOs.

Weld County, CO is heavily influenced by confined animal feeding operations and was excluded from this spatial analysis. The high variability between sites indicated that the current AMoN siting criteria (no major sources of NH_3 within 20 km) is appropriate, as sites nearby CAFOs would not be representative of a regional area. Excluding the Weld County sites, the median r^2 for the Fort Collins area sites was 0.44 (n=55). Including Weld County results in an r^2 of 0.17 (n=136). The Fort Collins data results in a reasonable interpolation distance of 30 km (70% of the variability explained).

Conclusions

The results of this study are consistent with the measured results we see from the AMoN annual average concentrations. The 2015 AMoN average concentrations from sites located in Illinois, Wisconsin, and Indiana were between 1.2 and 2.6 $\mu g\ m^{-3}$. The Midwest region is typically influenced by spatially homogenous sources (large crop fields, fertilizer applications). Conversely, the variability in concentrations in Colorado was significantly greater. Averages annual concentrations in CO ranged from less than 0.5 to 3.2 $\mu g\ m^{-3}$ in 2015 with greater influence from complex terrain and CAFOs in the foothills.

The results of this study may be used to assess the size of an AMoN site footprint for the bi-directional flux estimates. There is a need to address the spatial variability of the bi-directional flux on a regional scale. It is likely that long-range transport of NH_3 may occur in rural areas where acidic pollutant concentrations are relatively low. Understanding the spatial variability of NH_3 concentrations and deposition will help state and local agencies address PM2.5 formation and NAAQS exceedances.

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