Agricultural and Forest Meteorology 214-215 (2015) 380–392

Contents lists available at ScienceDirect

Agricultural and Forest Meteorology

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

Background concentrations and fluxes of atmospheric ammonia over a deciduous forest

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ARTICLE INFO

Article history:
Received 17 October 2014
Received in revised form 31 August 2015
Accepted 5 September 2015
Available online 16 September 2015

Keywords:
Forest–atmosphere interactions
Ammonia flux
Emission
Relaxed Eddy Accumulation
Gas-particle partitioning

ABSTRACT

Natural ammonia (NH_3) fluxes over terrestrial ecosystems are difficult to quantify because most measurement sites are influenced by nearby anthropogenic NH_3 sources. Furthermore, measuring the net exchange of NH_3 is challenging due to bi-directionality of the flux and the high reactivity of NH_3. In this study, we present two months of half-hourly NH_3 fluxes and concentrations measured using a Relaxed Eddy Accumulation system during late summer and fall 2013 above a remote forest site in the central Midwest in USA. Supplementary nitric acid (HNO_3) flux and size-resolved aerosol-N measurements are used to quantify the phase-partitioning and diagnose possible causes of upward NH_3 fluxes. Data from 2013 combined with previous NH_3 studies at this site indicate a seasonal background NH_3 concentration of spring: 0.92 ± 0.95, summer: 0.30 ± 0.39, autumn: 0.20 ± 0.26, and winter: 0.26 ± 0.1 $\mu g\, NH_3\text{-}N\, m^{-3}$. Air mass back trajectories from the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model did not indicate any directional bias in the measured NH_3 concentration confirming the absence of strong local sources of NH_3. The NH_3 fluxes were mainly upward (emission) and had a magnitude of up to 0.11 $\mu g\, NH_3\text{-}N\, m^{-2}\, s^{-1}$. The wetness of the forest surfaces (assessed using a proxy of time since precipitation) was found to be crucial in controlling both deposition and emission of atmospheric NH_3. Size resolved aerosol concentrations (of NH_4^+, NO_3^-, Cl^- and SO_4^{2-}) indicated that the aerosol and gas phase concentration of ammonia/ammonium were of similar magnitude but that the aerosol phase typically dominated. Nitric acid flux measurements showed periods of apparent upward fluxes, but they were not preferentially associated with upwards NH_3 fluxes indicating they may not have a common causality.

1. Introduction and objectives

Ammonia (NH_3) contributes to the atmospheric deposition of reactive nitrogen (N) to the Earths surfaces and is important in several environmental perspectives. Through deposition to sensitive ecosystems, NH_3 can cause eutrophication and acidification resulting in biodiversity loss. Through chemical reactions with acidic gasses and aerosols in the atmosphere, NH_3 contributes to aerosol formation and is thus linked to adverse human health effects and visibility degradation (Bobbink et al., 2010; Hertel et al., 2012; Sutton et al., 2011). Ammonia is principally emitted to the atmosphere from the agricultural sector as a result of animal husbandry, and storage and spreading of manure and mineral fertilizer (Skjøth and Geels, 2013), but non-agricultural sources such as sewage and vehicles can contribute a non-negligible fraction to local, regional and even national emissions (Sutton et al., 2013). Natural and semi-natural ecosystems most often function as a sink for NH_3, but a number of studies have reported bi-directional NH_3 fluxes over forests and other vegetative ecosystems (Hansen et al., 2013; Schjoerring et al., 2000; Sutton et al., 1997; Wyers and Erisman, 1998). A number of previous studies have documented and postulated causal mechanisms for upward fluxes of NH_3 over forests:

- Measurements over a beech forest in Denmark showed NH_3 emissions of up to 0.67 ± 0.28 $\mu g\, NH_3\text{-}N\, m^{-2}\, s^{-1}$ in the leaf fall period even in the presence of atmospheric concentrations of up to 2 $\mu g\, NH_3\text{-}N\, m^{-3}$ (Hansen et al., 2013). These high emission fluxes

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http://dx.doi.org/10.1016/j.agrformet.2015.09.004
0168-1923/

were suggested to be due to microbiological breakdown of leaf litter, but nearby agricultural sources of NH_3 upwind from the measurement site made it impossible to ascribe the emissions solely to the forest, as it is impossible to separate the contribution from agricultural NH_3 emissions or forest NH_3 emissions to the atmospheric NH_3 concentration.

- Pryor et al. (2001) conducted measurements over a mixed deciduous forest and presented evidence to suggest that evaporation of water vapor and particle bound nitrogen compounds from leaf surfaces was responsible for observed upward fluxes of nearly 0.06 $\mu g\, NH_3\text{-}N\, m^{-2}\, s^{-1}$.
- The stomatal compensation point controlled by the apoplastic ammonium (NH_4^+) and hydrogen ion (H^+) concentrations in the leaf has been shown to contribute to NH_3 release from natural ecosystems to the atmosphere (Massad et al., 2010; Schjoerring et al., 1998).
- Partitioning of N compounds between the gas and aerosol phases can have a significant effect on local budgets of atmospheric reactive N (Nemitz et al., 2004), and atmospheric flux divergence in the nitric acid (HNO_3), NH_3, and aerosol ammonium nitrate (NH_4NO_3) triad has also been postulated to be a cause of apparent upward NH_3 fluxes (Kramm and Dlugi, 1994; Nemitz and Sutton, 2004; Nemitz et al., 2004).

Given the importance of NH_3 to atmospheric chemistry and ecosystem function, there is a need for in situ data with which to:

(1) Evaluate atmospheric chemistry models (Flechard et al., 2011; Hansen et al., 2013) and satellite retrievals of atmospheric NH_3 concentrations (Pinder et al., 2011; Zhu et al., 2013).
(2) Evaluate NH_3 emission inventories (Reis et al., 2009).
(3) Characterize and improve understanding of the processes that dictate NH_3 exchange (Flechard et al., 2013; Hansen et al., 2013).

The first two research themes require the measurement locations to be representative of regional concentrations. However, in most of Europe, natural ecosystems cover relatively small areas and are often surrounded by intensive agricultural activities. This makes it difficult to isolate the natural process-level controls on the concentrations and fluxes of NH_3 over natural ecosystems, as the measurements will be influenced by local anthropogenic sources (Hansen et al., 2013). Thus, the measurements presented herein were undertaken in a relatively homogeneous and expansive forest in eastern North America. The third research theme is necessary to improve predictions of the exchange of NH_3 between forests and the atmosphere, but it requires both fluxes and concentrations to be measured. However, there remain considerable technical challenges to obtain accurate continuous NH_3 concentration and flux measurements at high temporal resolution due to the high reactivity and solubility of NH_3. Some existing measurement methods suffer from slow response time, high detection limits, and interaction between the gas and the instrument parts (Schwab et al., 2007). As a more recent alternative, Whitehead et al. (2008) evaluated laser absorption in combination with the eddy covariance method for measurements of NH_3 fluxes and found the method suitable, though it underestimated the flux by 64% in comparison with measurements using the Ammonia Measurement by ANnular Denuder with online Analysis (AMANDA) (Wyers et al., 1993) system in combination with the aerodynamic gradient method. The Wet Effluent Diffusion Denuder (WEDD) method, as employed in this study, uses the solubility of NH_3 to capture the gas in water for subsequent chemical detection of the liquid NH_4^+ (Sørensen et al., 1994). The performance of the WEDD approach is comparable to other approaches to sample the NH_3 concentration under environmental conditions. Fluxes are more challenging to measure, but the WEDD system approach can be used for this purpose in combination with the Relaxed Eddy Accumulation (REA) method (Hensen et al., 2009).

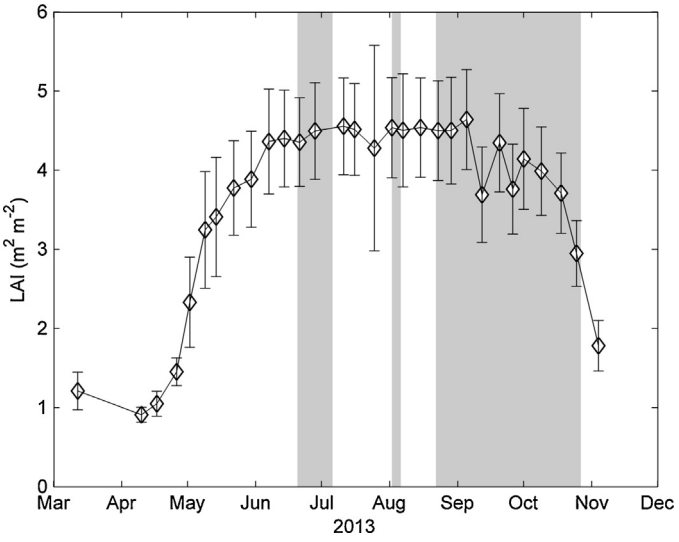

Fig. 1. Mean leaf area index (LAI) for MMSF during the growing season of 2013. Diamonds indicate the mean of LAI measurements conducted using a LI-COR-2200 at eight locations along three transects radiating from the tower. The vertical bars denote the standard deviation from the mean and thus represent the spatial variability in LAI along the three transects. The gray shading on the figure denotes the periods during which the atmospheric concentration and flux of NH_3 (c_{NH_3}) was measured.

The objective of this paper is to quantify the seasonal background atmospheric concentrations and exchange of NH_3 for a remote forest in southern Indiana, the Morgan-Monroe State Forest (MMSF), and to understand the process-level controls on the exchange of NH_3. Half-hourly NH_3 concentration and flux measurements were conducted over a mixed deciduous forest during late summer/autumn; 20 June–5 July, 2–6 August and during 22 August–27 October 2013 (marked with gray in Fig. 1) During a shorter intensive campaign between 18 September and 12 October, HNO_3 fluxes and size-resolved aerosol particle composition measurements were also undertaken and are used to diagnose possible causes of the observed upward NH_3 fluxes.

To contextualize the NH_3 observations and examine the degree to which the concentration measurements at this site in southern Indiana are regionally representative we also present data from prior field campaigns at this site, and two-weekly time-integrated data from the National Atmospheric Deposition Program (NADP) measurements at Bondville, IL, approximately 200 km northwest of the measurement site. We also compute 8-times daily, 24-hour airmass back trajectories for a terminating height of 500 m at MMSF, using the HYbrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler et al., 2013) based on 12 km resolution output from the North American Mesoscale Forecast System (NAM).

2. Methods

2.1. Site description

The measurements presented herein were conducted on the 46-m AmeriFlux tower in Morgan-Monroe State Forest (MMSF) located at 39°53′ N, 86°25′ W in the southern Indiana, USA (Pryor et al., 2001). MMSF is a secondary successional broadleaf forest dominated by the deciduous tree species tulip poplar (*Liriodendron tulipifera*), white oak (*Quercus alba*), sassafras (*Sassafras albidum*) and sugar maple (*Acer saccharum*) and covers 9712 hectares. Beyond the limits of the forest, the surrounding land cover is