Ammonia Flux Measurements above a Corn Canopy using Relaxed Eddy Accumulation and a Flux Gradient System

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Highlights:

- Inter-comparison of relaxed eddy accumulation and flux gradient measurements
- Strong correlation between the two NH_3 flux measurement methods
- Peak NH_3 flux measured with both systems six days after fertilizer application
- Two elevated emission periods influenced by urease inhibitor and environmental conditions

Abstract

Studies of NH_3 flux over agricultural ecosystems in the USA are limited by low temporal resolution (typically hours or days) and sparse spatial coverage, with no studies over corn in the Midwest USA. We report on NH_3 flux measurements over a corn canopy in Central Illinois, USA, using the relaxed eddy accumulation (REA) and flux gradient (FG) methods, providing measurements at 4 h and 0.5 h intervals, respectively. The REA and FG systems were operated for the duration of the 2014 corn-growing season. Flux-footprint analysis was used to select data from both systems, resulting in 82 concurrent measurements. Mean NH_3 flux of concurrent measurements was 205 ± 300 ng m^{-2} s^{-1} from REA and 110 ± 256 ng m^{-2} s^{-1} from FG for all concurrent samples. Results from both methods were not significantly different at a 95% confidence level for all concurrent measurements. The FG system resolved NH_3 emission peaks at 0.5 h averaging time that were otherwise un-observed with 4 h REA averaging. Two early-season emission periods were identified (DOY 130-132 and 140-143), where the timing and intensity of such emissions were attributed to a combination of urease inhibitor, applied as a field-management decision, and localized soil temperature and precipitation. Given the dependence of NH_3 fluxes on multiple parameters, this study further highlights the need for increased spatial coverage and high temporal resolution (*e.g.,* < 1 h) of measurements to better understand the impact of agricultural NH_3 emissions on air quality and the global nitrogen cycle. Such measurements are also needed for evaluation of models describing surface-atmosphere exchange of NH_3.

Introduction

1.1 Reactive Nitrogen and Anthropogenic Ammonia

Continued population growth has resulted in increased demand for food, yielding perturbations to the global nitrogen cycle (Erisman et al., 2013). While the use of nitrogen-based fertilizers for food production has improved the ability to cultivate crops in nitrogen-limited ecosystems, emission of NH_3 from fertilized cropland results in adverse environmental effects (USEPA, 2011). According to the U.S. EPA 2014 National Emission Inventory (NEI), 95% of total atmospheric NH_3 emission is attributed to anthropogenic sources (USEPA, 2017). Fertilizer application accounts for 28% of anthropogenic NH_3 emissions in the USA and is regionally varied based on land use (USEPA, 2017). Fertilizer application accounts for 52% of anthropogenic NH_3 emission in Illinois (USEPA, 2017). NH_3 volatilized from cropland to the atmosphere reacts with acidic compounds in the atmosphere to form particulate matter with diameter $\leq$ 2.5 μm ($PM_{2.5}$), causing adverse health effects and contributing to wet and dry deposition of reactive nitrogen that can lead to deleterious environmental effects including waterway eutrophication and soil acidification (Galloway et al., 2008; Green et al., 2012).

Urea-ammonium nitrate (UAN) solution is commonly used as a synthetic nitrogen fertilizer in Illinois (UI, 2009). After application of UAN to bare soil, the urease enzyme, present in soils, catalyzes the hydrolysis of urea to NH_4^+ and, depending on weather conditions and soil properties (*e.g.*, moisture, temperature, and pH), results in part of the applied reactive nitrogen volatizing as NH_3 to the atmosphere (Fenn and Hossner, 1985). However, the use of N-(n-butyl)-thiophosphoric triamide (nBTPT) urease inhibitor can reduce NH_3 emission by inactivating the site of the enzyme responsible for catalyzing the hydrolysis reaction (Watson et al., 1994). Chadwick et al. (2005) reported reductions of NH_3 emission from UAN ranging from 15 – 71% (44% mean reduction, number of samples = 10) when nBTPT urease inhibitor was used on grasslands and cereal crops.

Successful SO_x and NO_x regulatory policies combined with increased use of nitrogen-based fertilizers have led to an increased amount of NH_3 and NH_4^+ in the environment, as evidenced by a shift of reactive nitrogen deposition in the USA from oxidized to reduced nitrogen (Li et al., 2016). However, further regulation of NO_x and SO_x may no longer be cost beneficial when compared with control of NH_3 emissions to reduce atmospheric particulate matter concentration (Pinder et al., 2007). Improved understanding of NH_3 fluxes is important to more fully characterize their impact on the global nitrogen cycle, develop targeted strategies for emission reductions, and reduce the formation of secondary air pollutants (Flechard et al., 2013; Li et al., 2016).

1.2 Quantification of Ammonia Flux

The U.S. EPA Science Advisory Board (SAB) has called for increased direct measurements of NH_3 emission from agricultural cropland to better understand nitrogen fertilizer use efficiency (NFUE) and to identify regions and crop types that contribute significantly to anthropogenic NH_3 emissions to the atmosphere (USEPA, 2011). Limited measurements of NH_3 emissions contribute to poor temporal and spatial representation of NH_3 in regional air quality models (Appel et al., 2011) and restrict the ability to evaluate models developed to predict NH_3 emissions (Balasubramanian et al., 2017). Existing models (Bash et al., 2010) and measurements using accumulation methods (Walker et al., 2013; Nelson et al., 2017) suggest that NH_3 emissions are not temporally uniform and are influenced by local environmental conditions that can change on the order of minutes.

Measurement of biosphere-atmosphere NH_3 flux is challenging because NH_3 is readily absorbed by water and is reactive with acidic species in the atmosphere (Sutton et al., 2007), while gaseous NH_3 co-exists with particulate NH_4^+. Low concentrations of NH_3 previously observed at agricultural sites (*i.e.,* 0.5 – 4 μg m^{-3} two weeks after fertilizer application) (Nelson et al., 2017) limit the suitability of several fast response (10 Hz) detectors due to higher detection limits (0.10 μg m^{-3} NH_3 at 10 Hz with total accuracy of 0.14 μg m^{-3} NH_3 ± 10 %; Miller et al., 2014). Many reported measurements of NH_3 flux from agricultural crop systems rely on chemical adsorption and/or accumulating methods to quantify flux, resulting in temporal resolutions of hours or days (Myles et al., 2007; Walker et al., 2013; Nelson et al., 2017).

Recent improvements to instrument detection limits have resulted in several demonstrations of fast-response closed eddy covariance (EC) systems for measuring NH_3 flux from cattle feedlots (Ferrara et al., 2014; Sintermann et al., 2011). However, such systems are limited by reactivity of NH_3 in sample lines and inlets that can affect high-frequency response and result in underestimation of NH_3 flux (Ferrara et al., 2014). Open-path EC systems are a promising alternative to improve fast-response measurement as they avoid the potential interference from sampling lines. Such a system was used for measurement of NH_3 flux at cattle feedlots, with a limit of detection for NH_3 flux of 1.3 ± 0.5 ng m^{-2} s^{-1} over a 30-min average (Sun et al., 2015). However, the exposed optics make long-duration measurement (*i.e.,* > 1 day) in an open agricultural field challenging due to fouling of the optical cell by airborne dust and insects (Miller et al. 2014).

Improved temporal resolution of measurements during the early-season period are needed to better understand the variability of NH_3 flux (Walker et al. 2013) and to quantify the benefit of urease inhibitors on reducing NH_3 volatilization at the field scale (Nelson et al., 2017). Further, existing process-based models to describe surface-atmosphere exchange of NH_3 at sub-hourly timescale, such as SURFATM-NH_3 (Personne et al., 2009) which simulates the bi-directional exchange of NH_3 with vegetation and Volt'air-NH_3 which simulates NH_3 fluxes from bare soil (Génermont and Cellier, 1997; Garcia et al., 2012) require field-scale measurements at similar timescales for evaluation. Walker et al. (2013) suggested that existing NH_3 models may be least suited to accurately predict emissions during the first month after fertilizer application, when emissions are highest and most variable.

1.3 Research Motivation and Significance

In this paper, we present an inter-comparison of NH_3 flux measurements above a corn canopy in Central Illinois, USA, using relaxed eddy accumulation (REA) and the flux gradient (FG) measurement methods. This inter-comparison provides an important understanding of the efficacy of the FG method when compared with the REA method, which has been more extensively used for NH_3 flux measurement in varied ecosystems (Zhu et al., 2000; Meyers et al., 2006; Myles et al., 2007) and in Central Illinois, USA (Nelson et al., 2017). FG can yield sub-hourly temporal resolution of NH_3 flux and has been used to measure NH_3 fluxes over a variety of managed agricultural ecosystems including grassland

(Sutton et al., 2001; Spindler et al., 2001; Milford et al., 2009), corn (Harper and Sharpe, 1995), triticale (Loubet et al., 2012) wheat (Personne et al., 2015), and unfertilized soybean (Myles et al., 2011). However, measurements at sub-hourly timescale have not been reported for corn managed under typical agricultural practices and under the micrometeorological conditions in the Midwest USA.

Enhanced temporal resolution of NH_3 flux measurements provided by FG is important to improve the understanding of the impact of localized environmental parameters on NH_3 flux intensity and to evaluate local and regional modeling of NH_3 flux (Flechard et al., 2013; Walker et al., 2013). Further, FG provides a beneficial method for characterizing diurnal patterns of NH_3 flux, which has not previously been reported in the literature for typical field-management practices in Illinois. This research inter-compares concurrent REA measurements of NH_3 flux over an intensively managed corn field in Central Illinois, USA (Nelson et al., 2017) with new 30 min averaged NH_3 flux measurements from a continuously operated FG system. These new measurements, and the inter-comparison of experimental methods, are important to improve our understanding of temporal variability of NH_3 fluxes. They are also important for micrometeorological measurement method evaluation and further development of such methods in diverse environments in terms of climate, topography, and land use. These results can be used to further enhance NH_3 emission model evaluations and to improve understanding of the impact of intensively managed agricultural ecosystems on air quality and the global nitrogen cycle.

2. Methods

2.1 Site Description and Field Management Practices

The field campaign was conducted during the 2014 corn-growing season at the University of Illinois at Urbana-Champaign (UIUC) Energy Biosciences Institute (EBI) Energy Farm in Illinois, USA. A complete description of field management practices and geographic features of the Energy Farm and surrounding area, and methods for measuring crop height and leaf area index (LAI) is presented in Nelson et al. (2017). Briefly, the Energy Farm was subdivided into four 200 m x 200 m research plots, each planted with one of either miscanthus, switchgrass, restored prairie, or corn. This research was conducted at the corn plot (hereafter referred to as the “study plot”) during the first year of a corn-corn-soybean rotation. No artificial irrigation was applied to the study plot.

The study plot was treated with 168 kg-N ha^{-1} as 28% urea-ammonium nitrate (UAN) fertilizer in water (Illini FS: Urbana, IL), 7.0 L ha^{-1} pre-emergent herbicide (Lumax®, Syngenta: Basel, Switzerland), and 3.36 kg ha^{-1} urease inhibitor (Agrotain® DRI-MAXX [0.0625 % w/w of UAN], Koch Agronomic Services: Wichita, KS, USA), on May 6, 2014 (DOY 126). The study plot was tilled and machine-sown with corn (Dekalb®, DKC64-69, Monsanto: St. Louis, MO) at 76 cm row spacing to a seeded population of 86,000 plants ha^{-1} in the afternoon on DOY 126. Herbicide (Roundup® Powermax, Monsanto: St. Louis, MO) was applied at 1.6 L ha^{-1} on June 6, 2014 (DOY 157) and additionally spot applied as needed.

2.2 NH_3 Flux Measurements

The REA system was setup and operational in the afternoon on DOY 126, 4 h after corn planting at the study plot. The FG system was setup over the following two days, and was operational on DOY 129. The study plot was serviced with two 20 A electrical circuits, both of which were required to operate the computers and pumps associated with the measurement systems. The REA and FG systems were 5 m apart at the center of the study plot, fully surrounded by corn (Figure 1).

Figure 1: The relaxed eddy accumulation (left tower) and flux gradient (right tower) measurement systems were located 5 m apart in the center of the study plot.

2.2.1 Relaxed Eddy Accumulation System

The REA system used for this field campaign is described by Nelson et al. (2017), but a brief description is provided here for improved clarity. Additionally, an evaluation of closure between REA measurements reported in Nelson et al. (2017) and modeled outputs using the DeNitrification DeComposition (DNDC) model is presented in Balasubramanian et al. (2017), where agreement between modeled and measured results was found to be best during the first 30 days after fertilizer application.

The mean vertical flux from REA, $\overline{F_{REA}}$ (ng m^{-2} s^{-1}), is estimated using Equation 1:

$$\overline{F_{REA}} = \beta\sigma_w\left(\overline{C^{\uparrow}} - \overline{C^{\downarrow}}\right) \tag{1}$$

where β is the REA coefficient (unitless), σ_w is the standard deviation of the vertical wind velocity, C is concentration (ng m^{-3}), overbars denote time averaging, and ↑ and ↓ denote up- and down-draft measurements, respectively. The REA coefficient is estimated from 10 Hz measurements of temperature from a sonic anemometer using Equation 2:

$$\beta = \frac{\overline{w'T'}}{\sigma_w\left(\overline{T^{\uparrow}} - \overline{T^{\downarrow}}\right)} \tag{2}$$

where w is vertical wind speed (m s^{-1}), T is temperature (K), and primes (‘) denote instantaneous deviations from the mean. The Eddy Accumulation (EA) method, originally introduced by Desjardins (1972), required that sample flow rates in up- and down-draft reservoirs be controlled proportionally with vertical wind speed. Businger and Oncley (1989) “relaxed” the EA method requirement by introducing the REA coefficient. The REA coefficient is a proportionality constant that accounts for the impact of vertical wind speed while sampling at a constant flow rate, thereby eliminating the complication associated with proportional sampling flow rates.

The REA system was operated intermittently throughout the growing season, with more sampling concentrated during the first 30 days following fertilizer application. No REA measurements were made during precipitation events to avoid aspiration of water into the denuders. REA samples were collected from 07:30 – 11:30 and 12:00 – 16:00 (all times are reported as local) to represent average meteorological conditions and avoid sampling during atmospheric stability transitions at dawn and dusk. The REA system was not used to collect nighttime samples as it is not expected to perform well during highly stable atmospheric conditions (Fotiadi et al., 2005).

Gas flow and switching of denuders during updraft, downdraft, and deadband conditions was controlled via a system similar to the one described by Meyers et al. (2006) with a field computer running the open source program SONIC.C (version 2.6.0, NOAA ATDD, SONIC program for Linux, Oak Ridge, TN). Flow rate through the denuders was fixed at 20.0 L min^{-1} using a mass flow controller (MFC) (model GFC371, Aalborg: Orangeburg, NY). The control system was connected to a three-axis ultrasonic anemometer (model 81000VRE, R.M. Young Company: Traverse City, MI) measuring wind speed in three directions (u, v, and w) and sonic temperature (T), at 10 Hz.

Phosphorous acid coated annular denuders (model URG-2000-30x242-3CSS, URG Corp: Chapel Hill, NC) were used to collect NH_3 in the REA system. All denuders were coated, extracted, and analyzed at the National Atmospheric Deposition Program (NADP) Central Analytical Laboratory (CAL). CAL used quality assurance procedures to mitigate potential contamination of samples (NADP, 2012). At least one laboratory blank and one field blank were used for every 20 denuders prepared. Four denuders were used for each REA sampling run: one each for updraft, deadband, and downdraft conditions and one as a field blank. Each REA sampling run lasted at least 4 h, guided by the analytical detection limit for NH_4^+ and typical ambient NH_3 concentrations in the area (Nelson et al., 2017).

2.2.2 Flux Gradient System

The FG technique is theoretically described by analogy to Fick's laws of diffusion, with an assumption that turbulent transfer is analogous to molecular diffusion. The turbulent flux is therefore proportional to the product of the mean vertical mixing ratio gradient and the vertical eddy diffusivity, K (Baldocchi at al., 1988). By assuming mass and energy are transported by the same eddies, eddy diffusivities are assumed equal among scalars and heat in the atmosphere. Hence, the FG technique assumes that the eddy diffusivity of each tracer gas is identical to the measured eddy diffusivity of heat (Hicks and Wesely, 1978). Based on this assumption, K is determined directly by combining the measured eddy covariance flux of temperature (F_H) and gradient measurements of temperature and concentration. Thus, the NH_3 flux from FG (F_{FG}) is calculated using Equation 3:

$$F_{FG} = -K_H \left(\frac{\Delta C_{NH_3}}{\Delta z}\right) = F_H \left(\frac{\Delta C_{NH_3}}{\Delta T}\right) \tag{3}$$

where K_H is the eddy diffusivity for sensible heat (m^2 s^{-1}), ΔC_{NH3} is the difference in NH_3 concentration (ng m^{-3}) between two measurement heights, Δz is the vertical distance between the two measurement points (m) and ΔT is the corresponding difference in temperature (K). Eddy covariance measurements of temperature flux were used to determine K_H (Myles et al., 2011).

The FG system is graphically depicted in Figure 2. The vertical distance between the two measurement heights was kept constant (Δz = 1.3 m) with a lowest initial measurement height of z = 0.4 m above the ground prior to corn emergence. Sampling height was adjusted with an automated exchange mechanism (AEM) (REBS Inc.: Bellevue, WA). The AEM design was similar in principle to that described by Gay and Fritschen (1979). After emergence, measurement height was adjusted weekly such that z = 0.2 m and 1.5 m above the canopy.

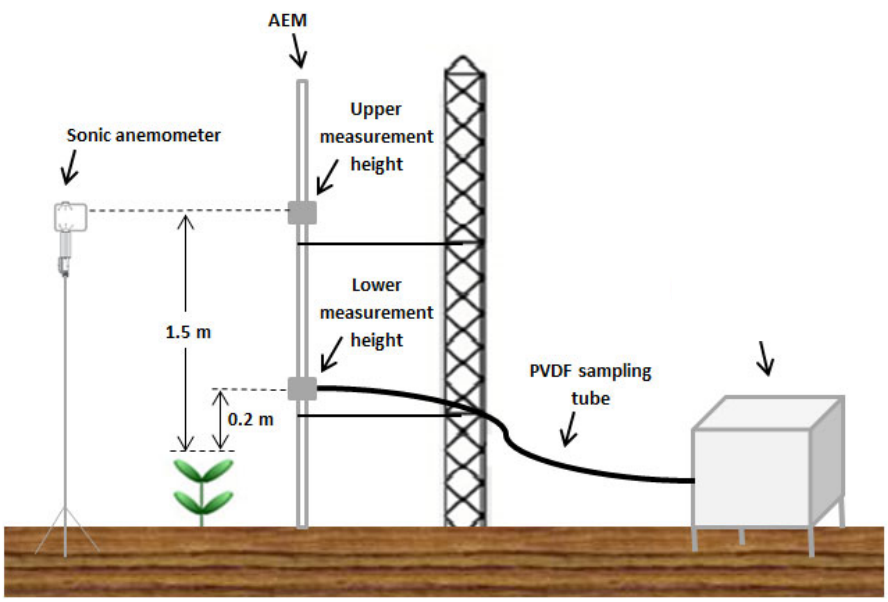

Figure 2: Schematic of the flux gradient (FG) sampling system with an automated exchange mechanism (AEM), cavity ring down spectrometer (CRDS), and polyvinylidene fluoride (PVDF) sampling tube.

In order to determine K_H, the sensible heat flux was measured by eddy covariance using a sonic anemometer (model 81000 VRE, R.M. Young: Traverse City, MI) placed at 1.5 m above the canopy. Temperature and three-dimensional wind speed (*u, v, w*; m s^{-1}) were measured with the sonic anemometer at 10 Hz using a custom Linux-based acquisition program developed by the NOAA Atmospheric Turbulence and Diffusion Division (Oak Ridge, TN) (Meyers et al., 1996). Measurements of temperature at the lower and upper measurement heights were made with resistance thermometers (1000 Ω Platinum Thermometer, Thermometrics Corp.: Northridge, CA) housed in aspirated radiation shields (model 43502, R.M. Young: Traverse City, MI) to minimize solar heating effects. 30-min average values of K_H were calculated using Equation 4:

$$K_H = -\frac{\overline{w'T'}}{(\Delta T/\Delta z)} \tag{4}$$

Concentration of NH_3 was measured using a cavity ring-down spectroscopy (CRDS) instrument (model G2103, Picarro Inc.: Santa Clara, CA) starting at the lower height for 7 min then switching to the upper height for 8 min and reversing the timing (i.e., 8 then 7 min at lower and upper heights, respectively). The lower detection limit of this instrument for NH_3 is < 0.06 μg m^{-3} with an accuracy of (± 5 % of reading + 0.35 μg m^{-3}) at a 300 s averaging time. CRDS is a laser absorption technique, which measures the lifetime of photons reflected between two mirrors in an optical cavity and determines the sum of sample extinction between the cavity mirrors, enabling quantification of NH_3 concentration by the strength of near-infrared absorption. (Scherer et al., 1997). The advantage of this method is that it allows absorption measurements using very long optical path lengths (effective path length up to 20 km) while maintaining a closed optical cell to enable single point measurements and limit contamination (Moosmüller et al., 2005).

The CRDS system was connected to a rotary pump (model 0523, Gast Manufacturing Inc.: Benton Harbor, MI) sampling at 70 L min^{-1}. The CRDS and pump were housed in an air-conditioned enclosure unit in which the temperature was adjusted to 10 °C below ambient to prevent overheating. The CRDS was calibrated by the manufacturer. Additionally, the calibration was verified using a short polyvinylidene fluoride (PVDF) vented inlet tube, and zero and span compressed gas cylinders according to manufacturer directions. The zero check was performed with ultrahigh purity nitrogen (99.999%) and the span adjustment was performed using 715.8 μg m^{-3} (1030 ppb ± 5 %) NH_3 (NIST-traceable reference gas; Air Liquide: Plumsteadville, PA). The zero and span checks were within the tolerance of the manufacturer's calibration with offset of ~0.8 ppb and span of ~1135 ppb.

An inlet tube was used to transfer air to the CRDS because it was housed in an enclosure and was situated in an agricultural field. Due to the high water solubility and polarity of NH_3, the choice of the sampling tube material was carefully investigated. PVDF was selected for use as the tubing material based on an experimental study by Vaittinen et al. (2014) that found it to be the least adsorbent polymer of five tested. An 8 m PVDF sampling tube (25.4 mm OD, 22.2 mm ID, McMaster-Carr: Elmhurst, IL) was used for the inlet line. The sampling tube was warmed with heating tape to 5 °C above ambient temperature to prevent condensation and limit NH_3 loss. The sampling tube was attached to the AEM allowing vertical movement.

NH_3 fluxes were continuously monitored (24 h/day) during the first three months of the 2014 corn-growing season (DOY 129 – 212), starting two days after fertilizer application and planting. NH_3 concentrations were averaged over 30 min. Due to precipitation events that blocked the sonic anemometer, 1.5% of overall samples were not collected. Furthermore, data corrections were conducted to limit interference from water vapor (Martin et al., 2016) and due to increasing pressure drop across the CRDS internal filter over time due to aspirated particulate dust, which contributes to increased response time. The response time of the NH_3 system was measured at the beginning and end of the corn-growing season, then corrected using the method of McCarthy (1973), based on a least squares exponential curve fit. The response time for the correction ranged from 4.8 min to 10.5 min. NH_3 data were smoothed to remove noise using a cubic spline filter. Data were further processed by removing measurements where the magnitude of the measured NH_3 flux exceeded the population mean by more than five standard deviations (SD). The use of five SD was compared with three SD as a cutoff prior to processing. Five SD was selected because of the relatively small difference in total data removed when compared with three (i.e., of 1458 data points remaining after footprint correction, 1447 data points remained after applying five SD and 1409 data points after applying three SD). This was further guided by a goal to limit exclusion of data associated with short-term (< 1 h) emission peaks.

NH_3 flux was calculated in 30 min averages (FG_{30min}) using the FG system. In order to account for possible NH_3 stickiness and response time, after filtering and correcting for the time constant, the final 3 min of each subsampling period were used for analysis (i.e., 6 min at each height per half hour period). Subsequently, 240 min average fluxes (FG_{240min}) were calculated from these data to compare with the timescale of REA measurements. FG_{240min} was calculated as a moving boxcar average, where averages were only calculated if FG_{30min} samples existed for the duration of the 240 min period.

2.3 Flux Footprint Analysis

Flux footprint was calculated for all REA and FG sampling periods using the EddyPro software package (Version 5.1.1, LI-COR: Lincoln, NE) (Nelson et al., 2017). The footprint parameterization described by Kljun et al. (2004) was used as the default option for footprint estimation. This method is only valid within a certain range of micrometeorological parameters. When measurements were outside this range, the crosswind integrated model by Kormann and Meixner (2001) was used.

Footprint was calculated for NN% = 10%, 30%, 50%, 70%, and 90% distances, where NN% distance corresponds to the calculated radius (r) of the area that contributed NN% of the total measured flux. The flux footprint calculation was used to select REA and FG samples where significant measured NH_3 flux originated from within the study plot (i.e., 70% and 90%). Samples were selected by comparing the 70% and 90% footprint distances corresponding to the shortest boundary of the study plot, r = 100 m. For example, if $r_{70\%} <$ 100 m for a particular sample, it was selected for further analysis.

2.4 Inter-comparison of REA and FG Measurements

All REA and FG measurements were compared to determine the total number of concurrent measurements after qualification using both the 70% and 90% footprint distance. For any 4 h REA measurement, an FG measurement was considered to be concurrent if there were at least 3 h overlapping data. This data qualification procedure based on footprint analysis ensures that reported data are representative of fluxes from the study plot and mitigates the influence of NH_3 emissions from neighboring fields.

Data were analyzed to investigate correlation and closure between concurrent F_{REA} and $F_{FG240min}$ data. The Pearson correlation coefficient ($Correl(REA, FG)$)was calculated for all concurrent measurements using Equation 5:

$$Correl(REA, FG) = \frac{\sum(F_{FG240min} - \overline{F_{FG240min}})(F_{REA} - \overline{F_{REA}})}{\sqrt{\sum(F_{FG240min} - \overline{F_{FG240min}})^2 \sum(F_{REA} - \overline{F_{REA}})^2}} \quad (5)$$

A nonparametric Wilcoxon ranks sum test was also used to evaluate whether there was statistically significant difference among the two measurement methods at a 0.95 confidence level (Walker et al., 2013).

3. Results

3.1 Canopy Development

Plants were first visible on May 12 (DOY 132), with peak canopy height of 308 cm ± 10 cm measured on July 25 (DOY 206). The canopy reached peak LAI (6.1) on August 13 (DOY 225). Harvesting of the corn was completed on November 6 (DOY 310) with an average yield of 13.78 mt ha^{-1} (219.5 bu acre^{-1}), consistent with the average yield in Champaign County for 2014 of 13.59 mt ha^{-1} (216.5 bu acre^{-1}) (USDA, 2015).

3.2 Full-Season Flux Measurements

Data presented in this paper are available in the Illinois data bank (Nelson et al., 2018). Full-season NH_3 flux measurements from the REA and FG systems are presented in Figure 3A (. FG measurements in Figure 3A, reported as 30 min averages (FG_{30min}), are selected based on footprint according to the method described in Section 2.3.

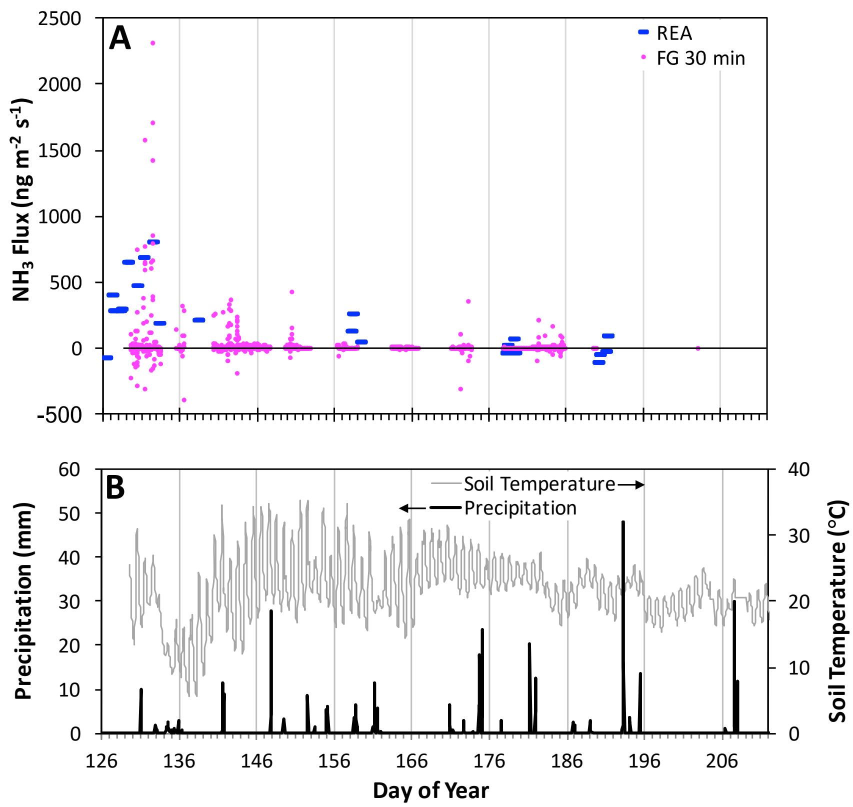

Figure 3: (A) NH_3 flux as measured using relaxed eddy accumulation (REA, 4 h integrated measurements) and 30 min averaged flux gradient (FG_{30min}) systems at the study plot for the full growing season (fertilizer application occurred on DOY 126). (B) Soil temperature (30 min average) and precipitation (30 min accumulated per event).

Mean soil temperature was 21.4 ± 4.4 °C, with lowest temperatures observed shortly following fertilizer application (DOY 133 – 140), when mean soil temperature was 13.5 ± 4.6 °C (Figure 3B). Total precipitation for all data reported in Figure 3B was 1082 mm as rain. Time series and descriptive statistics of additional select monitored variables are shown in Figures S1-S6 in supplementary material (SM), for the same period shown in Figure 3. No correlations were identified between NH_3 fluxes and the variables in SM. Turbulent mixing influences the accuracy of the measurements when micrometeorological methods are used and possibly affect the direction of fluxes. However, the extent to which these variables influence the observed variation of NH_3 fluxes is not easy to establish without a longer time series of continuous flux measurements, including measurements in- and above-canopy.

A summary of mean, maximum, and minimum NH_3 flux measured using REA and FG is presented in Table 1. FG results presented in Table 1 are divided into FG_{30min} and FG_{240min} data. Further, daytime and nighttime mean fluxes are provided for the FG method. REA results are not divided into daytime and nighttime measurements because REA was not used for nighttime measurements.

	NH_3 Flux (ng m^{-2} s^{-1})		
	REA	**FG_{30min}**	**FG_{240min}**
All data			
Mean	147 ± 284	23.9 ± 148	12.4 ± 73.2
Maximum	800	2312	1023
Minimum	-161	-400	-93
Daytime	- -	25.9 ± 93.5	17.0 ± 85.4
Nighttime	- -	-0.23 ± 0.23	0.1 ± 0.1
DOY 126 - 156			
Mean	431 ± 204	29.4 ± 169	24.0 ± 103
Daytime	- -	53 ± 159	34.4 ± 122
Nighttime	- -	-0.5 ± 9.0	0.4 ± 6.0
After DOY 156			
Mean	13.7 ± 99.2	0.8 ± 23.3	1.1 ± 7.1
Daytime	- -	1.4 ± 21.1	1.6 ± 7.7
Nighttime	- -	0.0 ± 2.0	-0.2 ± 1.8
Concurrent data			
Mean	205 ± 300	- -	110 ± 256

Table 1: Summary of all NH_3 flux measurements using relaxed eddy accumulation (REA) and flux gradient (FG) methods. FG_{30min} data correspond to 30 min average fluxes using FG, and FG_{240min} are 240 min averages. Data are further subdivided based on the first 30 days after planting (DOY 126-156) and the remainder of the season (after DOY 156), where DOY is "day of year".

Mean NH_3 fluxes over the entire growing season were 147 ± 284 ng m^{-2} s^{-1} and 23.9 ± 148 ng m^{-2} s^{-1} with REA and FG_{30min} data, respectively. The difference in mean flux measured with each system is attributed to the higher temporal resolution of the FG system, resulting in FG measurements across more environmental and atmospheric conditions, including measurements of deposition during nighttime and more measurements during daytime. Cumulative estimated N percent loss for the whole season was 5.8% and 6.0% from FG and the REA methods, respectively. Cumulative estimated N percent loss over the first 21 days after fertilizer application were 2.1% and 2.5% for FG and REA, respectively. Cumulative fluxes were estimated from mean daily fluxes measured with the FG and REA methods. The REA cumulative N loss percentage is lower than it has been reported before (Nelson et al., 2017) because the calculation method here was adjusted to account for negligible night time NH_3 fluxes, based on evidence from the FG continuous measurements, for the specific location.

3.2.1 Early Season Emission and Impact of Timescales

A similar emission trend was observed using both measurement methods. That is, peak NH_3 emission occurred during the first 30 days after fertilizer application followed by lower emissions for the remainder of the corn-growing season.

Figure 4 presents measurements using REA and FG_{30min} for the first 30 days following fertilizer application as well as precipitation and soil temperature data for the same time period.

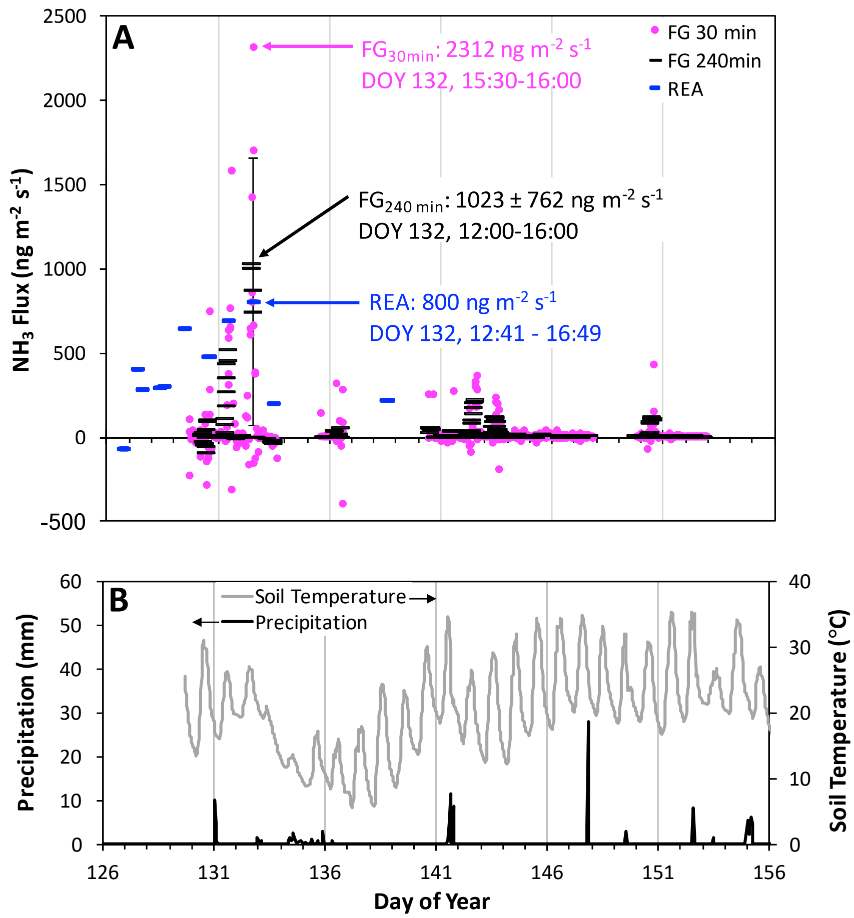

Figure 4: (A) Relaxed Eddy Accumulation (REA), 30-min Flux Gradient (FG_{30min}), and 240 min Flux Gradient (FG_{240min}) measurements of NH_3 flux during the first 30 days after fertilizer application. Error bars represent ± 1 standard deviation of the mean for the maximum FG_{240min} measurement only. (B) Soil temperature and precipitation during the same period.

Maximum observed NH_3 emission was 800 ng m^{-2} s^{-1} with REA and 2312 ng m^{-2} s^{-1} with FG_{30min}. The REA emission peak was observed during the 12:41 – 16:49 averaging interval on DOY 132 while the FG_{30min} peak was observed on the same day during the averaging period at 15:30 – 16:00. While the averaging periods for both maxima overlap, results from the FG_{30min} measurements indicate a high amount of variability. FG_{30min} measurements ranged from -157 to 2312 ng m^{-2} s^{-1} between 13:00 and 17:00 on DOY 132 with standard deviation of 762. Though the net flux during this time period was positive, there was one

FG_{30min} sample where deposition was observed (15:00 – 15:30). 10 mm precipitation as rain occurred on DOY 131, followed by a cold front, resulting in reduced soil temperature from a maximum of 30.9 °C in the afternoon on DOY 130 (

Figure 4B) to a maximum of 13.2 °C in the afternoon on DOY 134. Soil temperature did not return to 30.9 °C until DOY 141 in the morning.

To further investigate the effect of averaging time on the observed variability of NH_3 flux, REA measurements were compared with FG measurements averaged to 240 min intervals (FG_{240min}). Maximum emission was again observed in the afternoon on DOY 132 for both systems, where max REA flux was 800 ng m^{-2} s^{-1} from 12:41 to 16:49 and FG_{240min} maximum was 1023 ± 762 ng m^{-2} s^{-1} from 12:00 – 16:00. The REA and FG_{240min} flux maxima are not statistically different at 95% confidence level, due to the high standard deviation of the FG_{240min} measurement. The FG_{240min} peak was shifted earlier in the day by 0.75 h when compared to REA because emissions were generally higher earlier in the afternoon. As noted in section 2.2.2, FG_{240min} data used for this method comparison represent a subset of all FG_{30min} measurements because they only represent periods when eight consecutive FG_{30min} measurements were available during concurrent REA measurement periods.

The maximum 240 min averaged fluxes measured in this study are consistent with values of midday flux of 700 ± 1100 ng m^{-2} s^{-1}, reported by Walker et al. (2013). However, the FG system is capable of resolving the early season emission trend in higher resolution than previously reported in the literature using accumulating NH_3 flux measurement techniques (Nelson et al., 2017; Walker et al., 2013). This increased temporal resolution provides new information about non-stationarity in the NH_3 emission profile, where short-duration emission pulses vary in intensity by multiple orders of magnitude within a 4 h period. Further, the FG method provides an advantage over accumulating methods in that higher time resolution measurements subject to footprint distances that exceed the field boundary can be readily removed. It is therefore possible to collect more data when surface roughness and canopy height are low, corresponding to larger footprint distances. Such data are important to more fully understand the mechanism and profile of NH_3 fluxes.

Two different periods of elevated NH_3 emission were measured using the FG system: the first occurring during DOY 130 – 132, and the second during DOY 140 – 143. We attribute the timing and occurrence of these two distinct periods to environmental conditions (i.e., precipitation and soil temperature) and the use of urease inhibitor during fertilizer application. Previous studies have found elevated NH_3 emission to be correlated with higher temperatures (Sharpe and Harper, 1995; Balasubramanian et al., 2017). The highest FG_{30min} emission (2312 ng m^{-2} s^{-1}) was observed in the afternoon on DOY 132. This was followed by intermittent precipitation beginning at 23:00 on DOY 132 through 12:30 on DOY 136 resulting in a total rainfall during this period of 55 mm. Soil temperature subsequently reduced from 22.5 ± 2.8 °C on DOY 132 to a minimum of 11.6 ± 4.0 °C on DOY 137 (where temperatures are reported as average of 26 daytime measurements), and lower NH_3 emission was observed. Soil temperature then increased, reaching 24.4 ± 4.9 °C on DOY 140, concurrent with the second elevated emission period.

Beside meteorological conditions, the timing of the NH_3 emission peaks can be influenced by the properties of the applied fertilizer. Walker et al. (2013), observed two periods of elevated NH_3 emission following application of 134 kg N ha^{-1} UAN with

Agrotain®: one during the first week after fertilizer application (500 ng m^{-2} s^{-1}) and a second during the third week after fertilizer application (700 ng m^{-2} s^{-1}). Walker et al. (2013) attributed the emission profile to the effect of the urease inhibitor, where the first period is attributed to NH_4^+ fraction of the UAN volatilizing as NH_3, and the second period corresponds to reduced effectiveness of the urease inhibitor, resulting in hydrolysis of urea to NH_4^+ and subsequent volatilization as NH_3.

The profiles reported here and by Walker et al. (2013) differ from those reported by Rawluk et al. (2001) and Engel et al. (2011) during focused studies on the effect of urease inhibitor. In seven of eight field trials using chamber measurement methods, Rawluk et al. reported an emission profile with two periods of elevated NH_3 emission in only one trial. Engel et al. (2011) reported NH_3 emission peaks occurring 20 – 40 days after fertilizer application across 12 field trials, and presented no cases in which a bi-modal pattern of emission was observed. It is important to note that the study by Engel et al. was conducted over cold soils (-2 to 5 °C), so the magnitude of the time delay is expected to be increased when compared with this study. However, both of these studies were conducted using integrated sampling methods, with averaging intervals of one to four days by Rawluk et al., and five to seven days by Engel et al. Due to the short duration (< 2 days) of the first elevated emission period reported both in results presented here and by Walker et al. (2013), it is possible that such a peak would not have been observed using longer averaging intervals (*i.e.*, days). Further research is required to quantify the effect of urease inhibitor at the field scale relative to local environmental conditions.

3.3 Diurnal NH_3 Emission

A dynamic deadband was used in the REA system to increase the relative measured concentration of NH_3 in up- and down-draft denuders (Bowling et al., 1999). This approach helps to more effectively resolve NH_3 flux during turbulent conditions but can result in reduced data quality during neutral and stable nighttime conditions. As such, the REA method as used in this field campaign is not a suitable approach to measure nighttime NH_3 fluxes (Fotiadi et al., 2005).

Conversely, the FG method does not rely on turbulent eddies to trigger conditional sampling during up- and down-drafts. This enables the FG method to quantify flux across a broad range of atmospheric stability, including nighttime conditions. Additionally, the shorter 30 min averaging period reduces the impact of atmospheric non-stationarity on data quality. A clear diurnal pattern of NH_3 flux was observed, in which the highest positive fluxes and greatest variability in flux (as characterized by standard deviation) occurred during daytime hours. Mean NH_3 flux and standard deviation for each 30 min period across all qualified measurements are presented in Figure 5. We observe that there is a high variation in the measured fluxes. However, the measurements in general show upward fluxes, which are generally increasing in magnitude during the 09:00 – 16:00 period, while small upward or downward (depositional) fluxes are observed in the evening to early morning hours. This is consistent with the general understanding of bidirectional NH_3 fluxes, controlled by aerodynamic (r_a), quasi-laminar boundary layer (r_b), and bulk surface resistances (r_c), where r_a depends on meteorological and surface parameters (wind speed, air temperature, soil temperature, surface roughness length, leaf area index), r_b also depends on meteorology and NH_3 properties (i.e., solubility, reactivity) and molecular diffusivity and r_c on NH_3 compensation points in soil and in canopy (Wesely, 1989, Nemitz et al., 2000). Presence of dew and thin water layers on leaves contribute to NH_3 absorption and can account for the nighttime to early morning observed small upward or depositional fluxes (Nemitz et al.,2000). During daytime, increasing temperatures (affect dew evaporation, chemical equilibria at leaf, soil and stomatal resistance and the soil-air temperature differential), and changing atmospheric stability contribute to NH_3 fluxes shifting upwards, and their magnitudes to increase. It is not possible to infer from the measurements the relative influence of r_a, r_b, r_c. A low average flux is observed between 14:00 and 14:30 with an increased flux in the one hour period following that, with high variability. It is possible that a decrease in r_a and r_b due to a change in stability in mid-afternoon could result in higher dry deposition velocities (Liu et al., 2007).

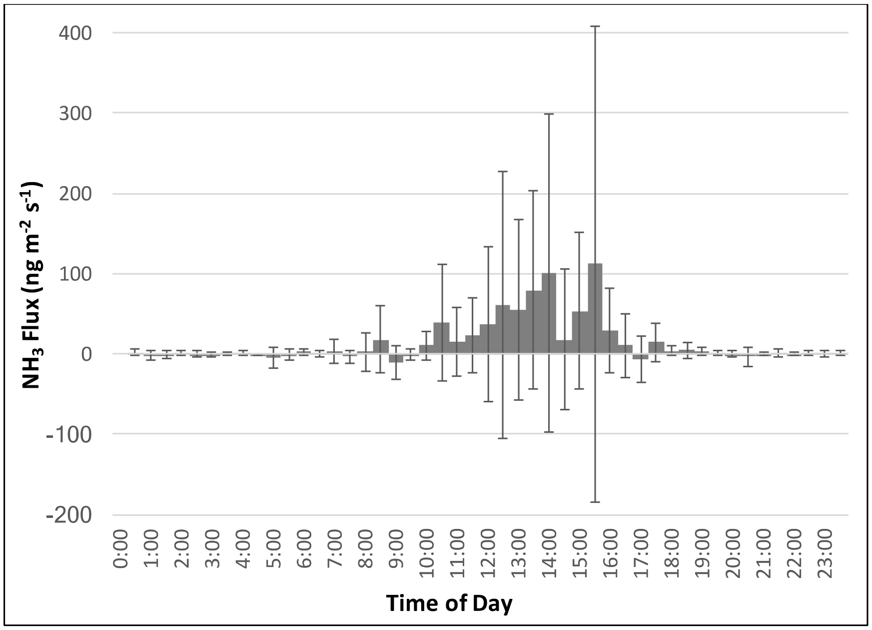

Figure 5: Diurnal pattern of NH_3 flux as measured using the flux gradient method, where solid bars indicate mean NH_3 flux during each 30 min period and error bars represent ± 1 standard deviation of the mean.

For the entire growing season, mean daytime FG_{30min} flux was 25.9 ± 93.5 ng m^{-2} s^{-1}, while mean nighttime flux was -0.23 ± 0.23 ng m^{-2} s^{-1}, where "daytime" is considered the interval with net radiation value greater than 12 Watts m^{-2} (EddyPro , Version 5.1.1, LI-COR: Lincoln, NE). When calculated for the first 30 days after fertilizer application (DOY 126 – 156), mean daytime flux was 53 ± 159 ng m^{-2} s^{-1}, compared to nighttime flux of -0.5 ± 9.0 ng m^{-2} s^{-1}. Following the first 30 days after fertilizer application, emission to the atmosphere was markedly lower during the daytime for the subsequent 30-day period (DOY 157 – 186), where daytime flux was 1.4 ± 21 ng m^{-2} s^{-1}, and 0.04 ± 2.1 ng m^{-2} s^{-1} during nighttime.

3.4 Inter-Comparison of Concurrent Measurements

After FG data qualification for $r_{90\%} < 100$ m and $r_{70\%} < 100$ m, remaining measurements were compared to determine total concurrent samples (Table 2).

	Number of Measurements (N)		
	Total	$r_{70\%}$ < 100 m	$r_{90\%}$ < 100m
REA	39	23	22
FG	2782	1178	896
Concurrent (4 h)	10	10	7
Concurrent (30 min)	82	82	57

Table 2: Total number of relaxed eddy accumulation (REA) and flux gradient (FG) measurements, remaining qualified measurements after using 70% and 90% footprint distance, and concurrent REA and FG samples, where "4 h" indicates measurements were concurrent during the entire 4 h REA interval and "30 min" indicates a concurrent REA measurement occurred during a 30 min FG measurement.

The REA system was operated most regularly during the first 30 days after fertilizer application, as this was the period of greatest interest for NH_3 flux measurement (Nelson et al., 2017). Therefore, it was also expected that the most concurrent REA and FG measurements would occur during this part of the season. However, challenges associated with the operation of the FG system at the beginning of the season limited the total number of concurrent measurements during this period. For the 70% footprint condition, six concurrent measurements were collected between DOY 131-158, while three concurrent measurements were collected for the 90% footprint condition. Since the early-season period is of most interest for NH_3 emissions (Walker et al., 2013; Nelson et al., 2017), the 70% footprint condition was used for the purpose of method inter-comparison discussed in this section (Table 3).

	$\overline{F_{NH3}}$ (ng m^{-2} s^{-1})		
DOY	**REA** (Nelson et al, 2017)	**FG_{240min}** ($r_{70\%}$ < 100 m)	**FG_{240min}** ($r_{90\%}$ < 100 m)
131	682.1	379.1	
132	799.6	752.6	
133	191.3	-35.9	
157	-8.5	5.0	5.0
158_1	130.8	-0.2	-0.2
158_2	254.5	-0.5	-0.5
178_1	-36.6	-0.1	-0.1
178_2	14.3	-0.1	-0.1
179_1	71.2	0.04	0.04
179_2	-44.8	0.01	0.01
All	**205 ± 300**	**110 ± 256**	**0.6 ± 2.0**

Table 3: Summary of all concurrent relaxed eddy accumulation (REA) and flux gradient (FG) measurements. REA measurements were footprint-corrected according to Nelson et al., 2017. FG measurements were averaged to a 4 h interval, after 70% and 90% footprint qualification, where _1 and _2 indicate morning and afternoon measurements, respectively.

$Correl(REA, FG)$ for all concurrent $r_{70\%}$ measurements, averaged to the 4 h REA averaging interval, was 0.91, indicating a strong correlation between the flux trends observed with both systems at the timescale of REA measurement. Measurements from both systems were in agreement using the Wilcoxon rank sum test at a 0.95 confidence level.

Later season REA flux measurements (*i.e.,* after DOY 157) were lower when compared with DOY 126-157, with mean measured flux of 14 ± 99.2 ng m^{-2} s^{-1}. For concurrent samples during DOY 158-179, mean flux with REA was 57.3 ± 106 ng m^{-2} s^{-1}, compared to -0.50 ± 5.10 ng m^{-2} s^{-1} with FG_{240min}. The FG method did not further resolve flux variability with 30-min or 240-min measurements during this period ($\overline{FG_{30min}}$ = 0.8 ± 23.3 ng m^{-2} s^{-1}; $\overline{FG_{240min}}$ = 1.1 ± 7.1 ng m^{-2} s^{-1}).

3.5 Benefits and Limitations of Measurement Methods

The REA method has been well-documented in literature for use in measuring trace atmospheric fluxes of NH_3 from fertilized fields (Myles et al., 2007; Walker et al., 2013; Nelson et al., 2017). However, these field campaigns have either been focused on a short period (1 to 3 months) of the total growing season (Myles et al., 2007; Walker et al., 2013) or limited in total number of measurements (N = 35) across a full growing season (Nelson et al., 2017). This is largely due to the labor required to operate an accumulating system coupled with the need for subsequent laboratory analysis of samples. It is necessary when operating such a system to have personnel on site at the beginning and end of each measurement interval. Further, samplers must be prepared and extracted in a controlled laboratory environment and stored under refrigeration. While not insurmountable, these challenges add to the complexity of using a REA system, under realistic field conditions.

The FG system was designed for near-autonomous, continuous operation under field conditions, though visits were required on a weekly basis to adjust the AEM and reference sonic anemometer and install a clean inlet. However, the complexity of the FG system led to additional downtime, due to equipment malfunctions and required frequent maintenance and adjustment. The length of the sampling line, combined with repeated vertical movement of the AEM resulted in kinking of the sampling line on multiple occasions. Challenges with the sampling line heater also resulted in condensation of water in the sample lines during periods of high relative humidity. Future research focused on technical improvements of the system could resolve some of these issues.

Though the complete REA system does require more regular field visits for operation, it benefits from being relatively inexpensive (< $10,000 equipment and installation costs) to deploy in the field. When compared with the complete FG system (> $100,000 equipment and installation costs), the cost of deploying a REA system has significant advantages when seeking to measure NH_3 emissions from a diverse range of field conditions, crop types, and agricultural practices. However, for situations where it is desirable to obtain higher time resolution emission and deposition fluxes in the first several weeks after fertilizer application, the REA method cannot provide the high temporal resolution that is possible with FG.

4. Summary and Conclusions

This research presents the first inter-comparison of NH_3 flux measurements using relaxed eddy accumulation (REA) and flux gradient (FG) systems in the USA. This inter-comparison was conducted above an intensively managed corn canopy in Central, Illinois, USA, thereby providing important new data regarding NH_3 fluxes under meteorological conditions in this area. Use of the FG system enabled temporal resolution of early-season peak fluxes greater than those previously reported using accumulating measurement methods. Results from the REA and FG system were highly correlated, with Pearson correlation of 0.91 between the two systems, when measurements at the same averaging time (4 h) were compared.

The FG system resolved two distinct periods of elevated early-season emission (DOY 130 – 132 and DOY 140 – 143). This was made possible by the advantage of 30 min sampling and straightforward removal of data when large footprint conditions were observed. The ability to accurately quantify fluxes over the 4 h REA averaging interval was limited during the second elevated emission event due to high winds and low surface roughness. The two periods of elevated emissions are attributed to a combination of the effect of localized environmental conditions (*i.e.,* precipitation and soil temperature) and nBTPT urease inhibitor. Further research is needed to understand the extent of the impact of these factors on early-season emission and to improve evaluation of process-based models with increased temporal resolution (*i.e.,* < 1 h).

Inter-comparison of the two measurement methods indicated that both methods are in good agreement with respect to 4 h average NH_3 fluxes. The FG system was able to resolve temporal variability in 30-min intervals that was not possible using the REA system. However, it was also sensitive to mechanical failure and extreme weather conditions, which resulted in loss of data during the corn growth season. The REA method is labor-intensive and needs be supported by strict quality assurance and quality control procedures for measurement of the typically low ambient NH_3 concentrations. The integrated nature of REA sampling often necessitates long fetch that can be challenging to achieve in many field conditions. When taken with other measurement considerations such as cost of equipment and operation, it is clear that there are tradeoffs needing careful consideration before implementing the methods in different environments. In terms of the broader picture, the question remains open regarding how to upscale these local measurements to the regional scale given the influences of environmental parameters, fertilizer properties, and method introduced variation. It appears that further method development and inter-comparison in diverse climatic, topographical, and land-use environments are essential to assist improved understanding of the spatial and temporal variability of biosphere-atmosphere NH_3 flux from agricultural fertilizer application and to facilitate evaluation of numerical emission and air quality models.

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References

Appel, K. W., Foley, K. M., Bash, J. O., Pinder, R. W., Dennis, R. L., Allen, D. J., and Pickering, K., 2011. A multi-resolution assessment of the community multiscale air quality (CMAQ) model v4.7 wet deposition estimates for 2002–2006. Geosci. Model Dev. 4, 357-371.

Balasubramanian, S., Koloutsou-Vakakis, S., McFarland, D. M., and Rood, M. J., 2015. Reconsidering emissions of ammonia from chemical fertilizer usage in Midwest USA. J. Geophys. Res. Atmos. 120, 6232-6246.

Balasubramanian, S., Nelson, A., Koloutsou-Vakakis, S., Lin, J., Rood, M. J., Myles, LT. and Bernacchi, C., 2017. Evaluation of DeNitrification DeComposition model for estimating ammonia fluxes from chemical fertilizer application. Agr. Forest Meteorol. 237-238, 123-134.

Baldocchi, D. D., Hincks, B. B., and Meyers, T. P. (1988). Measuring Biosphere-Atmosphere Exchanges of Biologically Related Gases with Micrometeorological Methods. Ecology 69, 1331-1340.

Bash, J. O., Walker, J.T., Katul, G.G., Jones, M.R., Nemitz, E., and W. P. Robarge, 2010. Estimation of in-canopy ammonia sources and sinks in a fertilized zea mays field. Environ. Sci. Technol. 44, 1683-1689.

Bowling, D.R., Delany, A.C., Turnipseed, A.A., Baldocchi, D.D., Monson, R.K., 1999. Modification of the relaxed eddy accumulation technique to maximize measured scalar mixing ratio differences in updrafts and downdrafts. J. Geophys. Res. 104, 9121–9133.

Businger, J., and Oncley, S.P., 1990. Flux measurement and conditional sampling. J. Atmos. Ocean Tech. 7, 349-352.

Chadwick, D., Misselbrook, T., Gilhespy, S. Williams, J., Bhogal, A., Sagoo, L., Nicholson, F., Webb, J., Anthony, S., Chambers, B., 2005. WP1b Ammonia emissions and crop N use efficiency. Component report for Defra Project NT2605 (CSA 6579).

Desjardins, R.L., 1972. A study of carbon-dioxide and sensible heat fluxes using the eddy correlation technique. *PhD dissertation* Cornell University, 189 pp.

Engel, R., Jones, C., Wallander, R., 2011. Ammonia Volatilization from Urea and Mitigation by NBPT following Surface Application to Cold Soils. Soil Sci. Soc. Am. J. 75, 2348–10.

Erisman, J. W., Galloway, J. N., Seitzinger, S., Bleeker, A., Dise, N. B., Petrescu, A. M., Leach, A. M., and de Vries, W., 2013. Consequences of human modification of the global nitrogen cycle. Philos. T. R. Soc. B. 368, 20130116.

Fenn, L.B., Hossner, L.R., 1985. Ammonia Volatilization from Ammonium or Ammonium-Forming Nitrogen Fertilizers, in: Stewart, B.A. (Ed.), Advances in Soil Science. Springer New York, pp. 123–169.

Ferrara, R.M., Loubet, B., Decuq, C., Palumbo, A.D., Di Tommasi, P., Magliulo, V., Masson, S., Personne, E., Cellier, P., Rana, G., 2014. Ammonia volatilisation following urea fertilisation in an irrigated sorghum crop in Italy. Agr. Forest Meteorol. 195-196, 179–191.

Flechard, C.R., Massad, R.S., Loubet, B., Personne, E., Simpson, D., Bash, J.O., Cooter, E.J., Nemitz, E., Sutton, M.A., 2013. Advances in understanding, models and parameterizations of biosphere-atmosphere ammonia exchange. Biogeosciences 10, 5183–5225.

Fotiadi, A. K., Lohou, F., Druilhet, A., Serça, D., Said, F., Laville, P., and Brut, A., 2005. Methodological development of the conditional sampling method. Part II: quality control criteria of relaxed eddy accumulation flux measurements. Bound-Lay. Meteorol. 117, 577-603.

Galloway, J. N., Townsend, A. R., Erisman, J. W., Bekunda, M., Cai, Z., Freney, J. R., Martinelli, L. A., Seitzinger, S. P., and Sutton, M. A., 2008. Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. Science 320, 889-892.

Garcia, L., Génermont, S., Bedos, C., Simon, N.N., Garnier, P., Loubet, B., Cellier, P., 2012. Accounting for surface cattle slurry in ammonia volatilization models: the case of Volt'Air. Soil Sci. Soc. Am. J. 76, 2184-2194.

Gay, L. W., Fritschen, L. J., 1979. An exchange system for precise measurements of temperature and humidity gradients in the air near the ground. Hydrology and Water Resources in Arizona and the Southwest, 2986, 37-42.

Génermont, S., Cellier, P., 1997. A mechanistic model for estimating ammonia volatilization from slurry applied to bare soil. Agr. Forest Meteorol. 88, 145-167.

Green M. C., Chen L. W., DuBois D. W., and Molenar J. V., 2012, Fine particulate matter and visibility in the Lake Tahoe Basin: chemical characterization, trends, and source apportionment. J. Air Waste Manage., 62, 953-65.

Harper, L.A., Sharpe, R.R., 1995. Nitrogen Dynamics in Irrigated Corn: Soil-Plant Nitrogen and Atmospheric Ammonia Transport. Agron. J. 87, 669–675.

Hicks, B.B., and M.L. Wesely. 1978. An examination of some micrometeorological methods for measuring dry deposition. EPA Publ. EPA-600/7-78-116. USEPA, Research Triangle Park, NC.

Kljun, N., P. Calanca, M. W. Rotach, and H. P. Schmid., 2004. A simple parameterisation for flux footprint predictions. Bound-Lay. Meteorol. 112, 503-523.

Kormann R., Meixner F. X., 2001. An analytical footprint model for non-neutral stratification, Bound-Lay. Meteorol. 99, 207–224.

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

Liu S., Lu L., Mao D., Jia L., 2007. Evaluating parameterizations of aerodynamic resistance to heat transfer using field measurements. Hydrol. Earth Syst. Sci., 11, 769–783, www.hydrol-

Loubet, B., Decuq, C., Personne, E**.,** Massad, R.S., Flechard, C., Fanucci, O., Mascher, N., Gueudet, J.C., Masson, S., Durand, B., Genermont, S., Fauvel, Y., Cellier, P., 2012. Investigating the stomatal, cuticular and soil ammonia fluxes over a growing tritical crop under high acidic loads. Biogeosciences, 9 , 1537-1552.

Martin, N. A., Ferracci, V., Cassidy, N., and Hoffnagle, J. A., 2016. The application of a cavity ring-down spectrometer to measurements of ambient ammonia using traceable primary standard gas mixtures. Applied Physics B, 122(8), 219, doi:10.1007/s00340-016-6486-9.

McCarthy, J. 1973. A method for correcting airborne temperature data for sensor response time. J. Appl. Meteorol. 12: 211–214.

Meyers, T. P., Hall, M. E., Lindberg, S. E., Kim, K., 1996. Use of the modified Bowen-ratio technique to measure fluxes of trace gases. Atmos. Environ., 30, 3321 – 3329.

Meyers, T., Luke, W., Meisinger, J., 2006. Fluxes of ammonia and sulfate over maize using relaxed eddy accumulation. Agr. Forest Meteorol. 136, 203–213.

Milford, C., Theobald, M. R., Nemitz, E., Hargreaves, K. J., Horvath, L., Raso, J., Dämmgen, U., Neftel, A., Jones, S. K., Hensen, A., Loubet, B., Cellier, P., and Sutton, M. A., 2009. Ammonia fluxes in relation to cutting and fertilization of an intensively managed grassland derived

Miller, D.J., Sun, K., Tao, L., Khan, M.A., Zondlo, M.A., 2014. Open-path, quantum cascade-laser-based sensor for high-resolution atmospheric ammonia measurements. Atmos. Meas. Tech. 7, 81–93.

Moosmüller, H., Varma, R., Arnott, W. P., 2005. Cavity ring-down and cavity-enhanced detection techniques for the measurement of aerosol extinction. Aerosol Science and Technology, 39, 30-39.

Myhre, G., Shindell, D., Bréon, F.M., Collins, W., Fuglestvedt, J., Huang, J., Koch, D., Lamarque, J.-F., Lee, D., Mendoza, B., Nakajima, T., Robock, A., Stephens, G., Takemura, T. and Zhang, H., 2013. Anthropogenic and natural radiative forcing. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Myles, L., Meyers, T.P., Robinson, L., 2007. Relaxed eddy accumulation measurements of ammonia, nitric acid, sulfur dioxide and particulate sulfate dry deposition near Tampa, FL, USA. Environ. Res. Lett. 2, 034004.

Myles, L., Kochendorfer, J., Heuer, M. W., and Meyers, T. P., 2011. Measurement of trace gas fluxes over an unfertilized agricultural field using the flux-gradient technique. J. Environ. Qual. 40, 1359-65.

NADP (2012) Standard Operating Procedure for Preparation and Extraction of URG Denuders. SOP Number PR-4074, Revision 1.1.

Nelson, A.J., Koloutsou-Vakakis, S., Rood, M.J., Myles, L., Lehmann, C., Balasubramanian, S., Joo, E. Heuer, M., Vieira-Filho, M., Lin, J. 2017. Season-long ammonia flux measurements above fertilized corn in central Illinois, USA, using relaxed eddy accumulation. Agr. Forest Meteorol., 239, 202-212.

Nelson, A. J; Lichiheb, N.; Koloutsou-Vakakis, S.; Rood, M. J.; Heuer, M.; Myles, L.; Joo, E.; Miller, J.; Bernacchi, C. 2018. Data for Ammonia Flux Measurements above a Corn Canopy using Relaxed Eddy Accumulation and a Flux Gradient System. University of Illinois at Urbana-Champaign. https://doi.org/10.13012/B2IDB-0071156_V1.

Nemitz, E., M. A. Sutton, J. K. Schjoerring, S. Husted, and G. P. Wyers, 2000, Resistance modelling of ammonia exchange above oilseed rape, Agric. Forest Meteorol., 105(4), 405–425.

Personne, E., Loubet, B., Herrmann, B., Mattsson, M., Schjoerring, J.K., Nemitz, E., Sutton, M.A., Cellier, P. 2009. SURFATM-NH3: a model combining the surface energy balance and bi-directional exchanges of ammonia applied at the field scale. Biogeosciences, 6:1371–1388.

Personne, E., Tardy, F., Génermont, S., Decuq, C., Gueudet, J.-C., Mascher, N., Durand, B., Masson, S., Lauransot, M., Fléchard, C., Burkhardt, J., Loubet, B., 2015. Investigating sources and sinks for ammonia exchanges between the atmosphere and a wheat canopy following slurry application with trailing hose. Agric. For. Meteorol., 207, 11-23.

Pinder, R.W., Adams, P.J., Pandis, S.N., 2007. Ammonia Emission Controls as a Cost-Effective Strategy for Reducing Atmospheric Particulate Matter in the Eastern United States. Environ. Sci. Technol. 41, 380–386.

Rawluk, C.D.L., Grant, C.A., Racz, G.J., 2001. Ammonia volatilization from soils fertilized with urea and varying rates of urease inhibitor NBPT. Can. J. Soil. Sci. 81, 239–246.

Scherer, J. J., Paul, J.B., O'Keefe, A., Saykally, R.J., 1997. Cavity ringdown laser absorption spectroscopy: History, development, and application to pulsed molecular beams. Chem. Rev. 97, 25-51.

Sharpe, R.R., Harper, L.A., 1995. Soil, plant and atmospheric conditions as they relate to ammonia volatilization. Fertil. Res. 42, 149–158.

Sintermann, J., Spirig, C., Jordan, A., Kuhn, U., Ammann, C., Neftel, A., 2011. Eddy covariance flux measurements of ammonia by high temperature chemical ionisation mass spectrometry. Atmos. Meas. Tech., 4, 599-616.

Spindler, G., Teichmann, U. and Sutton, M.A., 2001. Ammonia dry deposition over grassland-micrometeorological flux-gradient measurements and bidirectional flux calculations using an inferential model. Quarterly Journal of the Royal Meteorological Society, 127, 795-814.

Sun, K. Tao, L., Miller, D.J., Zondlo, M.A., Shonkwiler, K.B., Nash, C., Ham, J.M., 2015. Open-path eddy covariance measurements of ammonia fluxes from a beef cattle feedlot. Agr. Forest Meteorol. 213, 193–202.

Sutton, M. A., Milford, C., Nemitz, E., Theobald, M. R., Hill, P. W., Fowler, D., Schjoerring, J. K., Mattsson, M. E., Nielsen, K. H., Husted, S., Erisman, J. W., Otjes, R., Hensen, A., Mosquera, J., Cellier, P., Loubet, B., David, M., Genermont, S., Neftel, A., Blatter, A., Herrmann, B., Jones, S. K., Horvath, L., F¨uhrer, E., Mantzanas, K., Koukoura, Z., Gallagher, M.,Williams, P., Flynn, M., and Riedo, M., 2011. Biosphere-atmosphere interactions of ammonia with grasslands: experimental strategy and results from a new European initiative, Plant Soil, 228, 131–145.

Sutton, M. A., Nemitz, E., Erisman, J. W., Beier, C., Bahl, K. B., Cellier, P., de Vries, W., Cotrufo, F., Skiba, U., Di Marco, C., Jones, S., Laville, P., Soussana, J. F., Loubet, B., Twigg, M., Famulari, D., Whitehead, J., Gallagher, M. W., Neftel, A., Flechard, C. R., Herrmann, B., Calanca, P. L., Schjoerring, J. K., Daemmgen, U., Horvath, L., Tang, Y. S., Emmett, B. A., Tietema, A., Penuelas, J., Kesik, M., Brueggemann, N., Pilegaard, K., Vesala, T., Campbell, C. L., Olesen, J. E., Dragosits, U., Theobald, M. R., Levy, P., Mobbs, D. C., Milne, R., Viovy, N., Vuichard, N., Smith, J. U., Smith, P., Bergamaschi, P., Fowler, D., and Reis, S., 2007. Challenges in quantifying biosphere-atmosphere exchange of nitrogen species. Environ. Pollut. 150, 125-39.

UI, 2009. Illinois Agronomy Handbook, 24th edition. University of Illinois Extension.

USDA (2015), Illinois Corn County Estimates, Available from: https://www.nass.usda.gov/Statistics_by_State/Illinois/Publications/County_Estimates/2014/IL_Corn_Production_by_County.pdf. Last Accessed September 2017.

USEPA (2011), Reactive Nitrogen in the United States: An Analysis of Inputs, Flows, Consequences, and Management Options. Available from: http://www.epa.gov/sab. Last accessed August 2017.

USEPA (2017), The 2011 National Emissions Inventory, Available from: http://www.epa.gov/ttnchie1/net/2011inventory.html. Last accessed September 2017.

Walker, J.T., Jones, M.R., Bash, J.O., Myles, L., Meyers, T., Schwede, D., Herrick, J., Nemitz, E., Robarge, W., 2013. Processes of ammonia air–surface exchange in a fertilized *Zea mays* canopy. Biogeosciences 10, 981–998.

Watson, C.J., Miller, H., Poland, P., Kilpatrick, D.J., Allen, M.D.B., Garrett, M.K., Christianson, C.B., 1994. Soil Properties and the Ability of the Urease Inhibitor N-(n-BUTYL) Thoiphosphoric Triamide (nBTPT) to Reduce Ammonia Volatilization from Surface-Applied Urea. Soil Biology and Biochemistry 26, 1165–1171.

Wesely, M. L., 1989. Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models, Atmos. Environ., 23, 1293–1304.

Vaittinen, O., Metsälä, M., Persijn, S., Vainio, M. and Halonen, L., 2014. Adsorption of ammonia on treated stainless steel and polymer surfaces. App. Phys. B, 115, 185-196.

Bobrutzki, von, K., Braban, C.F., Famulari, D., Jones, S.K., Blackall, T., Smith, T.E.L., Blom, M., Coe, H., Gallagher, M., Ghalaieny, M., McGillen, M.R., Percival, C.J., Whitehead, J.D., Ellis, R., Murphy, J., Mohacsi, A., Pogany, A., Junninen, H., Rantanen, S., Sutton, M.A., Nemitz, E., 2010. Field inter-comparison of eleven atmospheric ammonia measurement techniques. Atmos. Meas. Tech. 3, 91–112.

Zhu, T., Pattey, E., Desjardins, R.L., 2000. Relaxed Eddy-Accumulation Technique for Measuring Ammonia Volatilization. Environ. Sci. Technol. 34, 199–203.