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Open-path eddy covariance measurements of ammonia fluxes from a beef cattle feedlot

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ABSTRACT

Eddy covariance (EC) measurements of NH_3 fluxes from a cattle feedlot were made with a high-precision, fast-response (20 Hz) open-path laser-based sensor. The sensor employed a continuous wave, quantum cascade (QC) laser and targeted an isolated absorption feature of NH_3 at 9.06 μm. It was deployed on a 5-m tall flux tower beside a 22,000-animal cattle feedlot in Colorado, USA for two weeks. Sensible heat, latent heat, CO_2, and CH_4 EC fluxes were measured concurrently on the tower. The open-path NH_3 sensor showed a comparable time response to well-established commercial open-path sensors for CO_2 and H_2O. The average high-frequency flux loss over the measurement period was 6.6%, mainly resulting from sample path averaging. The sensor showed significant improvement over NH_3 EC fluxes measured by closed-path sensors. The measured NH_3 EC fluxes were well-correlated with latent heat EC fluxes. During the measurement period, the average daily NH_3 EC flux was 31.7 kg ha^{-1} d^{-1}. The flux-variance relationship was used to further validate the performance of the NH_3 EC flux measurement. A 1σ detection limit of 1.3 ± 0.5 ng m^{-2} s^{-1} for NH_3 fluxes measured in 30-min intervals was achieved in this field test. This suite of measurements enabled the evaluation of livestock NH_3 emissions at unprecedented temporal resolution and accuracy in the context of other important agricultural trace gases.

1. Introduction

Atmospheric ammonia (NH_3) is the dominant alkaline species in the atmosphere. It neutralizes gaseous nitric and sulfuric acids to form ammoniated aerosols, which cause human health hazards (Paulot and Jacob, 2014), degrade visibility, and modify the radiative forcing of the global climate (IPCC, 2013). Ammonia is also a key compound in the global nitrogen cycle. The deposition of NH_3 and ammoniated aerosols contributes to the critical exceedance of nitrogen loading in ecosystems in regions of intense agricultural NH_3 sources and threatens those ecosystems' health (Krupa, 2003). However, understanding of atmospheric NH_3 is limited, and current NH_3 emission inventories have high uncertainties due to a lack of observational constraints (Clarisse et al., 2009; Shephard et al., 2011). Livestock production is thought to be the largest source of NH_3 emissions globally. For example, in the National Emission Inventory (NEI), livestock production accounts for 54% of total U.S. NH_3 emissions (EPA, 2013). Comparisons between atmospheric modeling and satellite observations imply that NH_3 emissions are widely underestimated in U.S. agricultural regions (Clarisse et al., 2009; Heald et al., 2012; Schiferl et al., 2014; Zhu et al., 2013). Based on aircraft observations, NH_3 emissions from Southern California livestock production are estimated to be 3–20 times larger than emission inventories (Nowak et al., 2012).

Micrometeorological methods (e.g., aerodynamic gradient method (AGM), relaxed eddy accumulation (REA), path-integrated techniques coupled with backward dispersion models, and eddy covariance (EC)) are often thought as the most desirable methods to measure NH_3 emission fluxes from livestock farming activities, because they measure fluxes over large integrated footprint areas without disturbing the surface or the animals (Baum and Ham, 2009; Todd et al., 2011; Whitehead et al., 2008). When applying these methods, stationarity, adequate fetch, and chemical reactions that occur within the turbulent transport time scale need to

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be carefully considered. The EC method is the most direct, least empirical and least error-prone approach, but it requires that the response time and sampling frequency of the NH_3 sensor should be on the order of 10 Hz to resolve the fluxes carried by small eddies (Kroon and Hensen, 2007). Recently, high-resolution NH_3 sensors including tunable laser spectroscopy (Ferrara et al., 2012; Whitehead et al., 2008) and chemical ionization mass spectrometry (Sintermann et al., 2011) have demonstrated some success of NH_3 EC flux in the field. However, due to the strong surface affinity of NH_3 molecules, no existing closed-path NH_3 sensor can meet the optimal response time for EC flux measurements (~0.1 s). Sintermann et al. (2011) reported a short time constant of 0.77 s due to dynamic gas exchange within the closed-path system and a long time constant of 23.06 s due to adsorption/desorption even when heating the drift tube of a PTR-MS instrument to 170 ° C. Ellis et al. (2010) reported a short time constant of 0.4 s and a long time constant of 15 s for a QC-TDLAS instrument.

The adsorption and desorption of NH_3 to the instrument surfaces and sample tubing introduce significant damping of high-frequency signals and significant underestimation of fluxes in most potential measurement situations (Brodeur et al., 2009). Whitehead et al. (2008) compared NH_3 EC measurements from two 10 Hz laser spectrometers (QCLAS and TDLAS) and tested these against the aerodynamic gradient method. They found that the QCLAS underestimated the NH_3 flux by 47% for unexplained reasons. Ferrara et al. (2012) investigated methods to correct the flux underestimation, and they calculated that the flux loss ranged from 23% to 43% depending upon the correction method. Moreover, this underestimation could be dependent on flux magnitude, which further complicated the flux corrections (Sintermann et al., 2011).

In contrast to closed-path configurations, an open-path design avoids significant adsorption/desorption effects between NH_3 and the instrument surfaces and the consequent damping of high-frequency fluctuations, even when sampling high (100 s ppbv to ppmv) concentrations directly downwind of sources. There is no need to use a heavy and power-hungry sampling pump, thereby making the open-path configuration more portable and adaptable for continuous measurements at remote EC sites. Furthermore, the open-path techniques avoid filters and heated inlets that cause ambiguity between gas phase NH_3 and that derived from volatilization of ammoniated aerosols. Open-path EC fluxes of H_2O, CO_2 and CH_4 are routinely measured with commercial sensors from LICOR (McDermitt et al., 2011). Path-integrated, remote NH_3 measurements have been demonstrated by open-path FTIRs (Bjorneberg et al., 2009), DOAS (Mount et al., 2002; Volten et al., 2012), and TDLAS (Todd et al., 2011), but these sensing systems all require long path lengths rather than compact sensor footprints needed for EC flux measurements. In the field, open-path EC measurements also face the challenges of dust, precipitation, and spectroscopic/density influences from water vapor and temperature. Thus far, no field-based, open-path EC measurements of NH_3 have been demonstrated in the literature.

In this study, we demonstrate EC measurements of NH_3 fluxes using an open-path, quantum cascade (QC) laser-based sensor at a beef cattle feedlot. The sensor has recently been demonstrated in the field in non-EC applications and is capable of high-resolution, fast-response, and high-sensitivity measurements (Miller et al., 2014; Sun et al., 2014). The sensor of Miller et al., 2014 was modified with significant improvements to ensure its performance for field EC measurements. Sensible heat, latent heat, CO_2, and CH_4 EC fluxes were measured concurrently at the same site. The performance of the open-path NH_3 sensor was evaluated and compared with the other commercial sensors. The NH_3 EC flux was correlated with the other EC fluxes, and the flux-variance relationship was used to further validate the measurements. This suite of measurements enabled the evaluation of livestock NH_3 emissions at unprecedented temporal resolution and accuracy in the context of other important tracers.

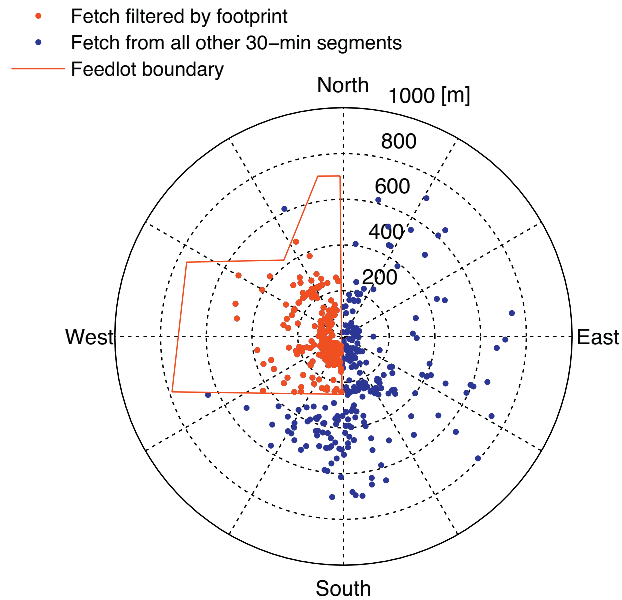

Fig. 1. Map of the feedlot boundaries (red line) and the upwind distances that recover 70% of the flux during the measurement period (points). The measurement tower was located at the origin. Red points denote periods that sampled within the feedlot boundary, while blue points show the fetches from all other 30-min sampling periods. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Materials and methods

2.1. Field site and flux footprint

Measurements were performed at a commercial cattle feedlot in northern Colorado with a cattle population of 22,000 head. The cattle were stocked at about 20 m^2 per animal and weighed between 300 and 600 kg depending on their age and days on feed. The crude protein in the animal diet was between 12.7 and 14.3%. The area receives about 360 mm of precipitation annually, and the terrain is flat with slopes less than 5%. The EC measurements lasted from November 12 to November 26, 2013. No significant precipitation was experienced during the measurement period except for a snow event on November 20–21, 2013. The measurement system was deployed on the east edge of the pens, providing a fetch in excess of 700 m when winds were from the prevailing westerly direction. Fig. 1 shows the outline of cattle pen area using geographic coordinates taken from a georeferenced digital map (ArcMap 10.2, Esri, Redlands, CA) with the sensors located at the origin of the plot. The sampling area consisted mainly of feedlot pens holding beef cattle. An analytical footprint model was used to calculate the source area contributing to the flux measurements (Hsieh et al., 2000). The displacement height and roughness length were determined following the methods reported in Baum et al. (2008), where the cattle density and average weight were very similar to this study. Only the one-dimensional flux density distribution was calculated as a function of upwind distance. The crosswind distribution was neglected because the average standard deviation of wind direction within each 30-min interval was found to be small ($13 \pm 6°$). An upwind distance that recovered 70% of the flux was used as the fetch requirement, and only cases with fetch inside the feedlot boundaries were used in the following analyses (Baum et al., 2008). Roads and alleys were included in the footprint filtering but these areas accounted for <10% of the total area within the feedlot