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Adaptation of a speciation sampling cartridge for measuring ammonia flux from cattle feedlots using relaxed eddy accumulation

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ABSTRACT

Improved measurements of ammonia losses from cattle feedlots are needed to quantify the national NH_3 emissions inventory and evaluate management techniques for reducing emissions. Speciation cartridges composed of glass honeycomb denuders and filter packs were adapted to measure gaseous NH_3 and aerosol NH_4^+ fluxes using relaxed eddy accumulation (REA). Laboratory testing showed that a cartridge equipped with four honeycomb denuders had a total capture capacity of 1800 μg of NH_3. In the field, a pair of cartridges was deployed adjacent to a sonic anemometer and an open-path gas analyzer on a mobile tower. High-speed valves were attached to the inlets of the cartridges and controlled by a datalogger so that up- and down-moving eddies were independently sampled based on direction of the vertical wind speed and a user-defined deadband. Air flowed continuously through the cartridges even when not sampling by means of a recirculating air handling system. Eddy covariance measurement of CO_2 and H_2O, as measured by the sonic and open-path gas analyzer, were used to determine the relaxation factor needed to compute REA-based fluxes. The REA system was field tested at the Beef Research Unit at Kansas State University in the summer and fall of 2007. Daytime NH_3 emissions ranged between 68 and 127 $\mu g\ m^{-2}\ s^{-1}$; fluxes tended to follow a diurnal pattern correlated with latent heat flux. Daily fluxes of NH_3 were between 2.5 and 4.7 $g\ m^{-2}\ d^{-1}$ and on average represented 38% of fed nitrogen. Aerosol NH_4^+ fluxes were negligible compared with NH_3 emissions. An REA system designed around the high-capacity speciation cartridges can be used to measure NH_3 fluxes from cattle feedlots and other strong sources. The system could be adapted to measure fluxes of other gases and aerosols.

1. Introduction

The effect of livestock production on air quality is a growing concern both nationally and globally; emissions of ammonia (NH_3) from animal feeding operations are of particular interest. A report by the National Research Council ranked NH_3 as the most important emission from confined animal feeding operations (CAFO) at regional and national scales (National Research Council, 2003). Regulations regarding regional haze prompted the U.S. Environmental Protection Agency (USEPA) to include NH_3 in the consolidated emission inventory reporting requirements because NH_3 is a precursor to the formation ofNH_4^+ aerosols, which contribute to $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5μm), a major contributor to regional haze (USEPA, 2002). Additionally, researchers have shown that NH_3 deposition can lead to soil acidification (ApSimon et al., 1987; Brunet et al., 1998), eutrophication and shifts in species composition (Bobbink et al., 1998; Pittcairn et al., 1998; Baron et al., 2000). Galloway et al. (2008) suggests that alteration of the nitrogen cycle by agriculture and other anthropogenic factors can have a cascading effect on the environment and human health at a global scale.

The livestock industry is the largest source of NH_3 emissions, accounting for an estimated 64% of global anthropogenic NH_3 emissions (Steinfeld et al., 2006), and cattle feedlots are a large component of the livestock industry. Nearly 30 million cattle on feed are marketed from U.S. feedlots every year and more than 80% of these animals are fed in the High Plains states of Texas, Oklahoma, Kansas, Nebraska, and Colorado (National Agricultural Statistics Service, 2004). Estimates of feed nitrogen for the cattle in this region total more than 2 million kg of N per day (Baum et al., 2008) and several field studies suggest that large fractions (>50%) of this nitrogen is lost to the atmosphere as NH_3 (Cole et al., 2006; Flesch et al., 2007; McGinn et al., 2007; Todd et al., 2008). Thus, obtaining accurate estimates of emissions from feedlots is important.

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Micrometeorological methods (e.g., eddy covariance (EC), relaxed eddy accumulation (REA)) are often considered the best methods for measuring fluxes from CAFOs (Shah et al., 2006) and are ideal in feedlot situations because they provide areally averaged flux measurements for large areas without disturbing the surface. Eddy covariance is the most desirable method because it provides a direct measure of flux; the flux density of a compound is expressed statistically as the covariance between deviations in the vertical wind speed and the mixing ratio of the compound of interest. This method is commonly used for measuring carbon dioxide and water vapor fluxes; however, high frequency measurements are needed, dictating the need for a fast-response analyzer (i.e., 10–20 Hz), which disallows its use for certain compounds including NH_3.

Relaxed eddy accumulation is an alternative to EC that avoids the need for a fast-response analyzer. Resolved by Businger and Oncley (1990), REA is a form of conditional sampling whereby samples of up- and down-moving eddies are sorted with high speed valves and can be analyzed with slower response analyzers or wet chemistry techniques. Mass flux, F (kg m^{-2} s^{-1}), is calculated as:

$$\overline{F} = \beta\rho\sigma_w\left(\overline{\chi^+} - \overline{\chi^-}\right) \quad (1)$$

where $\chi^{+/-}$ is the mixing ratio of the compound of interest for the up-moving and down-moving eddies, respectively (kg kg^{-1}); ρ is air density (kg m^{-3}); β is a dimensionless relaxation factor; σ_w is the standard deviation of the vertical wind speed (m s^{-1}); and overbars represent time-averages. In practice, a sonic anemometer measures the three-dimensional wind speed including the vertical velocity, w. If an eddy with upward trajectory is detected ($w > 0$), the upward valve is activated and air is diverted to the up-eddy reservoir. If an eddy with downward trajectory is detected ($w < 0$), the downward valve is activated and air is diverted to the down-eddy reservoir. Often, the difference between the mixing ratios of the up- and down-moving eddies is very small, so in practice, a deadband (db) is used. If the vertical wind speed is near zero ($|w| <$ db), air is not sampled, increasing the difference between the up-moving and down-moving mixing ratios. An overview of REA is provided by McInnes and Heilman (2005).

Several studies have successfully used REA to measure fluxes of various trace gases and aerosols (Beverland et al., 1996; Guenther et al., 1996; Valentini et al., 1997; Bowling et al., 1998; Christensen et al., 2000; Gaman et al., 2004). However, it is difficult to design an REA sampling system for NH_3 because of its reactive nature. A few studies have measured atmospheric NH_3 and NH_4^+ concentrations using glass denuder tubes (Ferm, 1979; Sutton et al., 2001). These systems have promise because they can selectively trap gaseous NH_3 only (excluding NH_4^+) and the NH_3 does not have to travel through tubing—it is immediately trapped by the coating of the glass denuders. Zhu et al. (2000) used denuder tubes in an REA system for measuring NH_3 fluxes from a fertilized corn field, but in CAFO situations where NH_3 concentrations are high (e.g., 300–600 μg m^{-3}), this is not feasible because the denuders would saturate within seconds.

A commercially available product that solves this problem is the Chemcomb Speciation Sampling Cartridge (model 3500, Thermo Scientific, Waltham, MA). The main components of this product are a well-characterized inlet and impactor plate with a 2.5 μm or 10 μm particle size cutoff, a series of glass honeycomb denuders, and a filterpack outlet. The honeycomb configuration of the denuders has the advantage of a very high capacity in a relatively small, compact package. Typically, each cartridge contains either two or four denuders with one (or two) denuders coated with a base for trapping acidic gases and one (or two) denuders coated with an acid for trapping basic gases. Because the denuders selectively trap gaseous compounds, the filterpack at the outlet can house various filters that will retain particulates, allowing for separate determination of gaseous and aerosol phases of compounds. The denuder-filterpack design offers flexibility in that virtually any compound can be measured if it can be trapped/retained by a denuder coating or filter paper, then extracted and quantitatively measured.

The objective of this research was to adapt the Chemcomb Speciation Sampling Cartridge to an REA system for measurement of NH_3 fluxes in a high-NH_3 environment. First, the configuration of the system is discussed. Then coating, handling, and capacity of the Chemcombs are described. Finally, results from preliminary field testing are presented.

2. Development of the REA sampling system

2.1. System configuration

The key to any REA system is designing a conditional air sampler that can independently collect up- and down-moving eddies. Typically, the REA sampler is collocated above the surface adjacent to a sonic anemometer. A data acquisition and control system reads the anemometer and, depending on the direction and magnitude of w, instantaneously activates valves that route gas samples into separate sample bags, denuders, or other types of chemical traps that receive either up eddies or down eddies. The design and function of the Chemcombs had to be carefully considered when adapting them to an REA system. Specifically, the Chemcombs were designed for a constant, continuous flow rate. In addition, the Chemcombs needed to be located within the system in a way that would minimize interaction of NH_3 with system components (i.e., tubing walls, pump, etc.). To address these issues, a circulating airflow design was used following the approach of Ham and Baum (2007) (Fig. 1). Air was circulated through the Chemcombs at 10 L min^{-1} with a dual head pump (R222-AT-AA1, Air Dimensions, Deerfield Beach, FL), and flow rates were controlled with mass flow controllers (0–15 L min^{-1}, AFCS36S-VADN5-C0A, Aalborg Instruments, Orangeburg, NY). Steel 1.0 and 0.5 L ballasts were located upstream and downstream of the pump, respectively. High-speed solenoid valves (091-0094-900, Parker Hannifin (General Valve Div.), Fairfield, NJ) were attached to the inlets of the Chemcombs using PTFE tees (K-31320-35, Cole Parmer, Vernon Hills, IL) and a small piece of 8 mm inner diameter vinyl tubing for a friction press fit into the Chemcomb nozzle. Speed of the valves was measured in the laboratory by measuring current flow in the solenoid coils using a resistor circuit and a digital oscilloscope. With 12 V excitation, the solenoid valves had opening and closing times of 1.1 and 1.7 ms, respectively. Valves were activated based on w, as measured using a sonic anemometer (CSAT3, Campbell Scientific, Inc., Logan, UT). Solid-state relay drivers (G4ODC5 and G4PB4R, Opto 22, Temecula, CA) connected to the control ports on the datalogger were used to energize the valves. When an up-moving eddy was detected, the up valve was activated and air was pulled through the up-moving eddy Chemcomb. Likewise, when a down-moving eddy was detected, the down valve was activated and air was pulled through the down-moving eddy Chemcomb. If the magnitude of w was less than the deadband, neither valve was activated. The NH_3-free air exhausted from the pump (scrubbed by the Chemcombs) was routed back to the "common" ports of the high-speed valves. The "normally open" ports of the valves were attached to the Chemcomb inlets so NH_3-free air was continuously recirculated through the Chemcombs unless the valves were activated. When the valves were activated and air was sampled, NH_3-free air was exhausted out the "normally closed" ports of the valves.