NH_3 emissions from grazing pasture following urea and urease inhibitor treatments

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Abstract
Ammonia (NH_3) volatilization to the atmosphere following urea based nitrogen (N) fertilizer application not only causes nutrient loss but also detrimentally impacts on the environment, our ecosystems, and contributes to global warming (as an indirect greenhouse gas). Here, we report our studies of quantifying NH_3 emissions from dairy pasture following urea application, and the effectiveness of a urease inhibitor in mitigating NH_3 loss. Two experiments were conducted in summer at Queensland (northern site) and autumn at South Australia (southern site) where urea was surface applied to pasture. A urease inhibitor (NBPT, applied with urea as Green ureaNV™) was added at the northern site. Open-path NH_3 laser concentration sensors were used to measure line-averaged concentrations along an open path downwind of the treatment plots. Ammonia fluxes were calculated using the inverse-dispersion technique (WindTrax). We found NH_3 flux increased following urea application and varied temporally at the two sites. Daily average NH_3 flux from dairy pastures fertilized with urea was 4.4 ± 0.46 and 6.4 ± 1.2 mg N m^{-2} h^{-1} for the northern and southern sites, respectively. Nitrogen loss as volatilised NH_3 from the urea application over the course of the experiments (12-15 days) accounted for approximately 40 and 60% of total applied N for the northern and southern sites, respectively. The difference between sites is likely attributed to the differences in N input, soil properties and microbial activity. The urease inhibitor reduced NH_3 emissions by approximately 71% compared to that from the urea treatment. The results in these studies also demonstrated that inverse-dispersion technique combined with the open-path lasers is able to measure NH_3 fluxes from large-scale field sites, and the open-path NH_3 laser has adequate detection resolution.

Key Words Open-path lasers, NH_3 emissions, grazing pasture, micrometeorological inverse-dispersion technique, urea fertilizer

Introduction
Applying nitrogen (N) fertilizer to grazing pasture is a common practice on dairy farms. Urea fertilizer applied to the soil surface can be hydrolysed rapidly to ammonia (NH_3). The NH_3 volatilization to the atmosphere can be a significant loss of valuable N from the fertilizer, and has negative impacts on the environment and human health, through the formation of aerosols (Sutton et al., 1998). In addition, the depositions of NH_3 downwind of farm can result in the emission of nitrous oxide (N_2O), a potent greenhouse gas, through the process of nitrification and denitrification, and eutrophication of waterways, consequently decreasing biodiversity in terrestrial ecosystems (Mosier et al., 1998; Smith et al., 2007). Application of fertiliser amendments has been used to reduce NH_3 emissions, e.g., urease inhibitor along with urea fertilizer is one of the options for increasing N fertilizer efficiency. It is well known that the urease inhibitor can control the hydrolysis of urea by inhibiting the urease enzyme activity (Chen et al., 2008).

Numerous studies on quantifying NH_3 emissions after N-fertilizer application have been conducted. Chamber techniques (e.g. wind tunnel) have been used to measure NH_3 emissions (Lockyer, 1984). The principle of chamber techniques is to draw air from a tunnel (cover above the fertilizer treated soil) to a flask which is filled with acidic solution that traps the NH_3, and then the NH_3 flux is determined by the calculation of NH_3 absorption. Micrometeorological techniques have the advantages of being a non-intrusive approach and representing real environmental conditions, e.g. the integrated horizontal flux (Denmead et al., 1998), and the passive sampling techniques (Leuning et al., 1985). The latter techniques are widely used in field measurements. However, the passive sampling techniques are labour intensive and have a low resolution of continuous measurements. Laubach et al. (2012) reported that the backward turbulence contributed to the uncertainty of flux measurement using this sampling technique. In the last two decades, a model based inverse-dispersion technique has become well-established with the simplicity of field flux measurements from a well-defined source area given by a single height concentration and wind statistics (Flesch et al., 1995). Furthermore, line-average NH_3 concentration sensors (e.g., lasers) have been commonly used in the large-scale measurements (up to 500 m path length), and no pump and tubing are required.

Here we report on two field studies to measure NH_3 emissions from dairy pasture following urea application at two locations (northern and southern sites) in summer and autumn using inverse-dispersion technique combined with open-path NH_3 concentration sensors. Furthermore, we added a urease inhibitor in conjunction with urea application at the northern site to investigate NH_3 reduction compared to NH_3 emissions with urea treatment.

Methods

Experimental site

Northern site

The first experiment was conducted at a research farm (27.54°S, 152.34°E), at the University of Queensland Gatton campus, 80 km west of Brisbane, Queensland from 23 November to 12 December 2013. The terrain was open and flat with short grass. The soil is typical silt loam, with a pH of 5.9 and 2.4% organic carbon (Table 1). No animals were grazed in this area. Two experimental plots (15 m radius) were constructed for urea treatment (U) and urea + urease inhibitor (NBPT) treatment (GU). The distance between these two plots was 50 m. Urea was applied to U plot surface at rate of 40 kg N ha^{-1} on 26 November 2013 and Green ureaNV^{TM} (40 kg N ha^{-1}, containing urea and urease inhibitor) was applied to GU plot surface on the same day. Ammonia measurements were made prior to the application and ended on 12 December. During the measurement period, the average maximum and minimum temperature was 30.2 and 16.0°C, respectively. The total rainfall was 79.4 mm (BOM, 2016a).

Two open-path NH_3 concentration sensors (NEO Monitors LaserGas, Norsk Elektro Optikk, Norway) were deployed using tuneable diode laser absorption spectroscopy technique. A transmitter combined with a single corner cube retro reflector measures the line-average NH_3 concentrations along the open path. The detection limit for NH_3 was less than 10 ppb at 100 m one way with response time of 1−2 seconds. One concentration sensor was placed 10 m west of U and GU plots separately, with each path length 80 m between transmitter and retro reflector at a height of 1.5 m above ground. One minute averaged concentrations of NH_3 were recorded. A weather station was set up 100 m south of the plots coupled with a three-dimensional (3-D) sonic anemometer (CSAT3, Campbell Scientific, Logan, UT, USA) at a height of 2.0 m above ground. Ten-minute average wind speed, wind direction, air temperature and air pressure were collected by a data logger (CR23X, Campbell Scientific, Logan, UT, USA) at a frequency of 10 Hz.

Southern site

The second experiment was conducted at a commercial dairy farm (38°01′S 140°55′E), 27 km southeast of Mount Gambier, South Australia between September and October 2014. The topography of the experimental site was open and flat and was covered by short grass. The soil is classified as clay loam, with a pH of 4.9 and 4.9% organic carbon (Table 1). There were no animals on site. One 25 m-radius experimental circle was created. Urea was spread to the pasture surface at rate of 50 kg N ha^{-1} on 30 September 2014. Measurements were made prior to the application and ended on 23 October. During the experimental period, the average maximum and minimum temperature were recorded at18.6 and 8.0°C, respectively. The total rainfall was 63.4 mm and average wind speed at 3 pm was 4.9 m s^{-1} (BOM, 2016b). The predominant winds during the study period were south-west-southwest.

Two open-path NH_3 Neo laser concentration sensors were used. One sensor was placed on the southern side and the other one was placed on the northern side of the plot; both were 5 m to the edge of the plot at a height of 1.48 m above ground. One minute average NH_3 concentrations were measured with the path length of 116 and 78 m for the laser on the north side and south side, respectively. A weather station coupled with a 3-D sonic anemometer (CSAT3, Campbell Scientific, Logan, UT, USA) was set up at a height of 2.47 m above ground, 300 m on the west side of the plot.

Data processing

At both sites two NH_3 concentration sensors were run side-by-side to calibrate the difference between the two sensors for two days prior to the flux measurements. Ammonia concentrations were not used for the flux calculation when light intensity of the concentration sensor was less than 10%. The wind turbulent parameters including wind friction velocity u_* (m s^{-1}), Obukhov stability length L (m), surface roughness length z_0 (m) and wind statistics were derived from sonic measurements. Following the filtering procedures

(Flesch et al., 2014), the error-prone data ($u_* < 0.05$ m s^{-1}, $|L| < 5$ m and $z_0 > 0.5$ m) were removed. Valid concentrations and wind variables were merged to 10-minue averages using SAS software (SAS 9.3, SAS Institute Inc., Cary, NC, USA). Ammonia fluxes from the experimental plot were calculated using the inverse-dispersion technique (WindTrax version 2.0.8.8, Thunder beach Scientific) given the line-averaged concentrations, wind turbulent statistics and defined source area.

Results

Northern site fluxes

Ten-minute average NH_3 fluxes show a temporal variation over the course of the experiment following urea application at the northern site (Fig 1A). As expected, NH_3 fluxes showed a significant correlation with wind speed and air temperature ($r = 0.50$, $P < 0.001$). Less than 10% of the flux measurements were observed before 6:00 or after 18:00, when the NH_3 losses were most likely negligible. The daily average NH_3 flux from U and GU plots were 4.39 ± 0.46 (mean ± SE, n = 228) and 1.25 ± 0.15 (mean ± SE, n = 529) mg N m^{-2} h^{-1}, accounting for 39.5 and 11.3% of total applied N, respectively (Table 1). In addition, we found GU reduced NH_3 volatilization by approximately 71.4% compared to U treatment. The N loss of total applied N in this study were higher than those reported on pastures in southern Victoria by Suter et al. (2013), which could be attributed to the weather conditions and soil properties.

Table 1. Nitrogen (N) input and soil properties obtained from the northern and southern sites.

	Northern site	Southern site
N input (kg N ha^{-1})	Urea:40 Green UreaNV^{TM}: 40	50
Soil Property		
Texture	Clay loam	Silt loam
pH ($CaCl_2$)	5.9	4.9
Organic carbon (%)	2.4	4.9
$^{\delta}$CEC (meq/100g)	26.0	11.5
NH_4^+–N (mg/kg)	3.5	8.9
NO_3^-–N (mg/kg)	2.1	28.8

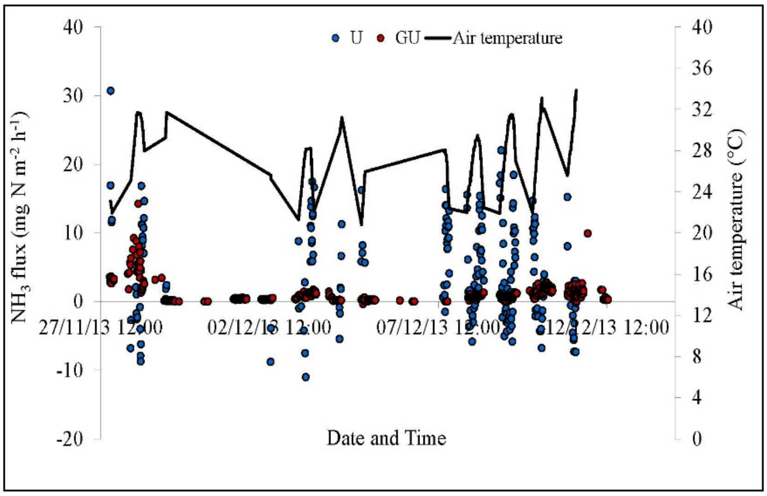
$^{\delta}$cation exchange capacity

Table 2. Daily average NH_3 fluxes from the northern and southern sites. Total N loss as volatilised NH_3 over the measurement periods (12-15 days) at the northern and southern sites are also calculated.

		Daily average NH_3 (mg N m^{-2} h^{-1})	N loss as volatilised NH_3 (%)
Northern site	Urea	4.39 ± 0.46	39.5
	Green UreaNV^{TM}	1.25 ± 0.15	11.3
Southern site	Urea	6.40 ± 1.23	59.5

The NH_3 background concentrations for the northern site were estimated by WindTrax using the point concentrations measured by passive samplers at a height of 2.9 m above ground, 50 m on the east of the GU plot during the same measurement period (Leuning et al., 1985). The samplers were replaced twice at 9:00 and 17:00 daily, the extract from samplers was analysed at laboratory to determine the concentrations over a period of measurement, such that two concentration measurements were obtained daily. In addition, the concentrations from upwind of U plot (northwest winds) measured by open-path NH_3 concentration sensor next to U plot were also used as the background concentrations of the experimental site. These estimates (samplers and concentration sensor) were adequate to reflect the variation in NH_3 background concentrations.

(A) Northern site



(B) Southern site

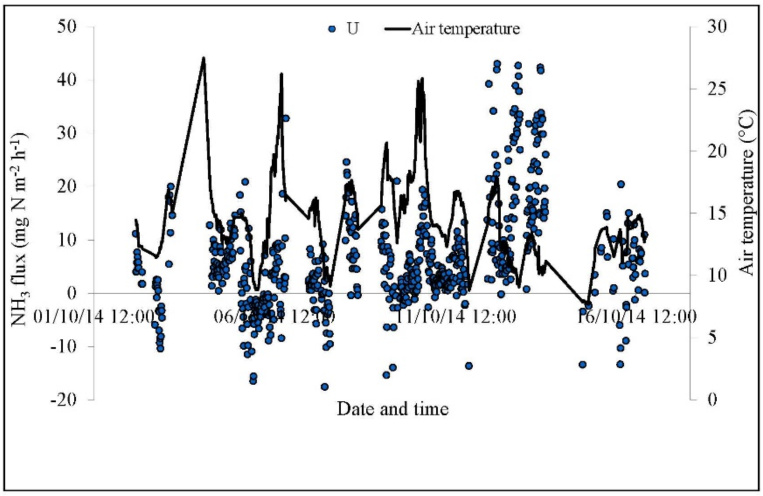


Fig. 1 A) Daily average NH_3 fluxes with urea (U) and Green UreaNV^{TM} (GU) treatments at northern site, B) with urea treatment at southern site. Air temperatures measured at both sites are also plotted.

Sothern site fluxes

Daily NH_3 fluxes from the plot at southern site showed temperature-dependent diurnal pattern with high emission at middle of day and low emissions at night-time (Fig. 1B). Average daily NH_3 flux was 6.4 ± 1.2 mg N m^{-2} h^{-1} (mean ± SE, n = 707) over 15 days measurement period (Table 2). This fits the range of 1−10 mg N m^{-2} h^{-1} reported by Ni et al. (2015) using inverse-dispersion combined with FTIR techniques. Nitrogen loss as NH_3 volatilization over the experimental period following urea application was 59.5% of the total applied N. This value was at the higher range of values reported in the previous studies, which could be likely associated with the soil properties and fertilizer types (Zaman et al., 2008).

Greater N loss was observed at the southern site likely due to higher N input, higher NH_4^+ and organic carbon contents of soils, and climatic conditions, and likely microbial activity associated with pasture species covered over the experimental site.

Conclusions

Ammonia fluxes increased following urea application, and a urease inhibitor reduced NH_3 volatilization. The inverse-dispersion technique combined with open-path NH_3 concentration sensors produced reliable measurements for large-scale field studies.

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