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Author/s:
Lam, SK;Suter, H;Bai, M;Walker, C;Mosier, AR;van Grinsven, H;Chen, D

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Title

Decreasing ammonia loss from an Australian pasture with the use of enhanced efficiency fertilizers

Author names and affiliations

Shu Kee Lam[a*], Helen Suter[a], Mei Bai[a], Charlie Walker[b], Arvin R. Mosier[a], Hans van Grinsven[c], Deli Chen[a*]

[a] School of Agriculture and Food, Faculty of Veterinary and Agricultural Sciences, The University of Melbourne, Victoria 3010, Australia

[b] Incitec Pivot Fertilisers, Seabreeze Parade, North Shore, Victoria 3214, Australia

[c] PBL Netherlands Environmental Assessment Agency, The Hague, The Netherlands

*Corresponding authors:

shukee.lam@unimelb.edu.au; delichen@unimelb.edu.au

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Abstract

Mitigating ammonia (NH_3) volatilization from intensive pasture systems is critical for environmental sustainability. However, field-scale evaluation on the potential of enhanced efficiency fertilizers (e.g. urease inhibitors and controlled-release fertilizers) in mitigating NH_3 volatilization is limited. Using a micrometeorological technique, we conducted two field trials to investigate the effects of Green UreaNV® (urea coated with the urease inhibitor *N*-(*n*-butyl)thiophosphoric triamide, NBPT) and polymer-coated urea (a controlled-release fertilizer) on NH_3 volatilization from an intensive rainfed pasture in southern Australia. We found that NH_3 volatilization from urea was 5.8 and 5.6 kg N ha^{-1}, respectively, in the autumn and spring trials, equivalent to 11–12% of the applied urea in each season. The use of Green UreaNV® and polymer-coated urea decreased the cumulative NH_3 volatilization by 45–55% and 80%, respectively. Taking into consideration the high environmental damage cost of NH_3 as found in the European Union, we hypothesize that both Green UreaNV® and polymer-coated urea can be cost-effective in mitigating NH_3 loss from this pasture. Our findings suggest that the extra cost of using these enhanced efficiency fertilizers for farmers is not compensated by the fertilizer N value of decreased NH_3 loss. However, from a societal perspective the extra cost for Green UreaNV® is likely outweighed by reduced environmental cost of NH_3. New fertilizer technology should be developed to improve the cost-effectiveness of polymer-coated urea to the farmers.

Keywords: ammonia volatilization, pasture, enhanced efficiency fertilizers, environmental damage cost, sustainability

1. Introduction

Ammonia (NH_3) emission is conducive to the formation of fine secondary particulate matter ($PM_{2.5}$) in the atmosphere (Schiferl et al., 2014; Wu et al., 2016). When deposited, NH_3 can

cause eutrophication of aquatic and terrestrial ecosystems, and nitrous oxide (N_2O) emission (Mosier et al., 1998; Galloway et al., 2008). The adverse impact of agricultural NH_3 emissions on human health and ecosystems has been estimated at € 10–120 billion per year in the European Union (van Grinsven et al., 2013) and updated to € 40–120 billion per year taking into account improved evidence for health impacts of NH_3 aerosols and impacts on marine ecosystems (van Grinsven et al., 2018). This highlights the urgency of NH_3 mitigation.

Ammonia mitigation measures include the use of enhanced efficiency fertilizers such as urea granules coated with a urease inhibitor, and controlled-release fertilizers, which are proven to be effective when used in various agricultural systems (e.g. Pan et al., 2016; Xia et al., 2017). Urease inhibitors are compounds that inhibit urease activity, thereby allowing the urea to move into the soil before hydrolysis, and subsequently reduce NH_3 volatilization (Chen et al., 2008). Controlled-release fertilizers such as polymer-coated urea control the release of N from urea via the polymer coating which acts as a physical barrier, thus satisfying plant requirements while maintaining low mineral N availability in the soil (Chen et al., 2008).

Fertilizer N application in the Australian dairy industries increased rapidly from 21 kg N ha^{-1} in 1990 to 94 kg N ha^{-1} in 2012 (Stott and Gourley, 2016); urea is the most commonly used N fertilizer in pastures (Havilah et al., 2005). However, there are limited field-scale studies on the quantification of NH_3 volatilization from Australian dairy pastures (e.g. Prasertsak et al., 2001; Eckard et al., 2003; Denmead et al., 2004), and very few on the potential of enhanced efficiency fertilizers in mitigating this important pathway of N loss (Suter et al., 2013; Lam et al., 2018). This is likely because a reliable quantification of NH_3 volatilization at the field scale requires the use of micrometeorological techniques (Denmead, 1983; Cichota and Snow, 2012), which involve huge labour and resource inputs, and large land area. In this study, we

conducted two field-scale measurements at a dairy pasture in a temperate region in southern Australia using a micrometeorological method. The objectives of the study were to investigate the effects of a urease inhibitor and a controlled-release coating on NH_3 volatilization from urea fertilizer in an intensive pasture system under open-air conditions, and to assess the economic and societal benefits of these enhanced efficiency fertilizers in mitigating NH_3 volatilization.

2. Materials and Methods

2.1 Experimental site

Field experiments were conducted on a temperate pasture dominated by perennial ryegrass (*Lolium perenne*) at Wye (38°01' S, 140°53'E), South Australia, Australia (Fig. 1), in autumn (6–26 May 2014) and spring (3–23 October 2014). The average minimum and maximum temperatures during the experimental period in autumn were 10.0°C and 18.7°C, respectively, and 7.5°C and 21.2°C in spring. The rainfall during the same period was 28.6 mm and 12.8 mm in autumn and spring, respectively (Bureau of Meteorology, 2013). A three-dimensional sonic anemometer (CSAT3, Campbell Scientific) was ~~established~~ placed on the field site to measure wind speed and wind direction during the experimental period. The soil at the site is classified as a Tenosol (Isbell, 1996) with 78% sand, 18% silt and 4% clay. The surface soil (0–0.10 m) had a pH ($CaCl_2$) of 4.9, and contained 4.9% organic C, 0.47% total N, 38.9 mg kg^{-1} NH_4^+-N and 28.8 mg kg^{-1} NO_3^- at commencement of the experiment.

2.2 Experimental design

Three treatments were included in this field experiment, viz. (i) urea (control), (ii) Green UreaNV® (urea coated with the urease inhibitor *N*-(*n*-butyl)thiophosphoric triamide, NBPT), and (iii) polymer-coated urea. Urea, Green UreaNV® and polymer-coated urea granules were

surface applied at a rate of 50 kg N ha^{-1} on 6 May and 3 October to a 50 m diameter circular experimental area, with one circular area assigned to each treatment. The adjacent experimental areas were separated by at least 100 m to avoid cross-contamination of NH_3 (Fig. 2).

2.3 *NH_3 volatilization*

A micrometeorological mass-balance method was used to determine the NH_3 flux from each treatment (Freney et al., 1985). Two passive NH_3 samplers (Leuning et al., 1985) were placed at 0.8 m above the ground surface on a mast located at the centre of each experimental area (Fig. 2). This height of 0.8 m is denoted as ZINST, or the stability independent height, which allows satisfactory determination of NH_3 loss irrespective of the atmospheric stability (Wilson et al., 1982; Denmead, 1983).

Background measurements were made from the two sides of the experimental area along the dominant wind direction, using two masts with the same height as the treatment circles. These masts were located at least 100 m from the edge of the closest circle (Fig. 2). Following fertilizer application in the first week, NH_3 measurements were made twice daily during the periods 0800–1700 h and 1700–0800 h (overnight). When the NH_3 flux gradually decreased in the second week, measurements were made daily, and every two to three days when the flux declined further in the third week. For each measurement, NH_3 captured in the Leuning samplers was eluted with 40 mL MilliQ water and analyzed for NH_4^+-N with a segmented flow analyzer (SAN^{++}, Skalar) (Keeney and Nelson, 1982). Ammonia flux for each measurement period was calculated as described by Freney et al. (1985) and Leuning et al. (1985), and summed over time to compute the cumulative emission.

2.4 *Soil N*

Soil samples (0–5 cm) were collected with a 2.5-cm (internal diameter) auger from the circular treatment areas daily or every second day for a week after fertilizer application, then every second or third day for the second week, and once in the final week. For each quarter of the treatment circles 10 soil cores were sampled and composited. A subsample (10 g) was taken from the composited sample and kept frozen at –20°C until extraction with 100 mL 2M KCl containing 10 mg L^{-1} phenylmercuric acetate. The extract was filtered with Whatman No. 42 filter papers and analyzed for urea and NH_4^+-N on the Skalar SAN^{++} segmented flow analyzer.

2.5 Statistical analysis

Data of soil urea and NH_4^+ contents were analyzed with MINITAB 16 statistical package using ANOVA. The least significant difference (l.s.d.) at $p = 0.05$ was used to compare the means between the treatments (four replications). It was not possible to replicate NH_3 measurements owing to the large area required for each treatment (~2,000 m^2), which is common for large-scale NH_3 flux measurements using the same micrometeorological technique (e.g. Turner et al., 2010). Nevertheless, this technique is robust for measurements of trace gas fluxes with uncertainty of within 15% (Denmead et al., 1998).

3. Results and discussion

3.1 Seasonal variation of ammonia volatilization

In the autumn trial, NH_3 volatilization peaked three days after application of urea (9 May) and remained low (< 0.5 kg N ha^{-1} day^{-1}) thereafter for all treatments (Fig. ~~1a~~3a). In contrast, NH_3 volatilization in the spring trial was steady and lasted for around 12 days after urea application (Fig. ~~1b~~3b). Ammonia volatilization is dependent on edaphic and environmental factors such as soil pH, wind speed and soil moisture (Freney et al., 1983). The volatilization

loss in our study site was driven by urea hydrolysis creating an alkaline hot spot (Du Preez and Burger, 1988) in this otherwise acidic environment (soil pH of 4.9). The average wind speed during the autumn and spring trials was 2.8 and 4.0 m s^{-1}, respectively. This is desirable for NH_3 volatilization because wind blows NH_3-rich air away from the soil surface and hence increases the NH_3 gradient between the air and the soil surface, and subsequently the rate of volatilization (Bolan et al., 2004).

In the autumn trial, the surface soil was sufficiently moistened by the heavy rainfall events (~50 mm on 3–5 May) before urea application on 6 May. The light rainfall events (1–2 mm) on 6 and 7 May allowed the urea granules to be dissolved but not diffused into the subsoil, resulting in an abrupt increase in NH_3 volatilization on 9 May (Fig. ~~1a~~3a). On 10 May the 7.6 mm rainfall was sufficient to wash the urea down in the soil, and ~~since then~~after that low NH_3 emission was ~~noted~~measured. This is supported by the decline in urea content from 6 May to 10 May (Fig. ~~2a~~4a). The effect of rainfall on NH_3 volatilization in our study is consistent with the findings by Sanz-Cobena et al. (2011), who found that low water input (3 mm rainfall) increased NH_3 emission but the emission became minimal when urea was washed into the subsoil by higher water input (7–14 mm rainfall).

In the spring trial, no rainfall events were recorded for four consecutive days prior to urea application on 3 October, rendering the surface soil dry, which delayed urea hydrolysis and NH_3 volatilization (Black et al., 1987). The light rainfall events on 6–8 October (3.6 mm) and 13 October (2.6 mm) triggered NH_3 volatilization (Fig. ~~1b~~3b). During these rainfall events the urea granules were gradually dissolved, as indicated by the increase in urea content from 6 October (Fig. ~~2b~~4b). Ammonia volatilization became minimal after the 6 mm rainfall on 16 Oct, which likely washed all the urea down into the soil profile. The above results suggest

that rainfall events played an important role in NH_3 volatilization from this pasture, and that the timing of fertilizer application should be adjusted based on the likelihood of adequate rainfall events so as to minimize NH_3 volatilization.

3.2 Mitigation of ammonia volatilization by enhanced efficiency fertilizers

The cumulative NH_3 emission for the urea treatment was 5.8 and 5.6 kg N ha^{-1} over the autumn and spring experimental periods, respectively, equivalent to 11–12% of the N applied. This percentage of N loss is comparable to the global average of 16% loss of N as NH_3 from surface applied urea in various agricultural systems (Pan et al., 2016). The N loss represents an economic loss to farmers of Australian dollars (AUD) 7.8 ha^{-1} (5.7 kg N ha^{-1} × 1.37 AUD kg^{-1} N) (Table 1). More importantly, the potential damage cost of NH_3 to human health (particulate matter) and ecosystem (eutrophication, biodiversity) in the European Union has been estimated at € 10–30 per kg NH_3-N (van Grinsven et al., 2013; 2018). Mitigation of NH_3 volatilization is therefore urgently needed to improve N use efficiency and environmental quality.

Ammonia volatilization can be decreased by adopting various mitigation strategies, as reported in recent global meta-analyses (Pan et al. 2016; Xia et al. 2017; Ti et al. 2019), including the use of urease inhibitors and controlled-release fertilizers. In our study, NH_3 emission in the autumn and spring trials was decreased by the Green UreaNV® (NBPT as the urease inhibitor) to 2.6 and 3.1 kg N ha^{-1}, respectively, representing a 45–55% reduction (Fig. ~~1~~3). Likewise, the polymer-coated urea decreased NH_3 volatilization to 1.1 kg N ha^{-1} in both trials, equivalent to an 80% reduction (Fig. ~~1~~3). The reduction induced by the urease inhibitor and the polymer-coated urea is similar to the ranges (53–54 and 57–68%, respectively) reported in the meta-analyses on NH_3 mitigation strategies (Pan et al., 2016; Ti et al., 2019).

The urease inhibitor NBPT inhibited urease activity and delayed urease hydrolysis (Sommer et al., 2004; Chen et al., 2008), thereby decreasing NH_3 volatilization. This is shown by the generally higher soil NH_4^+ content in the Green UreaNV® treatment than the urea treatment in both trials (Fig. 5a, b). ~~increase in~~The average soil NH_4^+ content increased from 107 (urea treatment) to 152 mg kg^{-1} (Green UreaNV® treatment) in the autumn trial ($p < 0.05$), and from 99 to 129 mg kg^{-1} in spring ($p < 0.05$). The relatively high soil NH_4^+ content (> 100 mg kg^{-1}) in this pasture was likely because NH_4^+ was retained in the soil, rather than being volatilized, in this acidic soil environment, combined with the relatively high background N due to past management of the pasture site. The polymer-coated urea, as a controlled-release fertilizer, slowed ~~down~~ urea release from the fertilizer granules (Chen et al., 2008). Consequently, throughout the experimental period, the NH_4^+ content under the treatment of polymer-coated urea (averaging 44 and 64 mg kg^{-1} in autumn and spring, respectively) was much lower than the urea treatment ($p < 0.05$) (Fig. 5a, b), and NH_3 volatilization was also decreased.

It is worth noting that fertilizers with urease inhibitor and controlled-release coatings are not widely adopted despite their effectiveness in mitigating NH_3 volatilization from various agricultural systems globally. One major obstacle preventing the wider adoption is that the extra cost of these fertilizer products (Table 1) may not secure productivity benefits (e.g. Suter et al., 2013; Nauer et al., 2018), as also observed in this field site (Suter et al., unpublished). This lack of productivity response in pastures has been attributed to non-limiting background soil N, unfavourable climatic conditions and differential responses of pasture species (Suter et al. 2013; Di and Cameron, 2016). We found that there were no financial benefits to farmers because the fertilizer N value of NH_3 saved by using Green UreaNV® and polymer-coated urea was lower than the extra cost of these products (Table 1).

This gap could be narrowed if these products can be produced at a lower cost or if subsidies are provided to farmers for using the products.

Nonetheless, a far more important but often ignored concern is the environmental sustainability of the system. As mentioned, the estimated environmental damage cost of NH_3 is € 10–30 per kg NH_3-N (van Grinsven et al., 2013). We performed a simple economic assessment for this Australian pasture based on the increase in fertilizer cost and the decrease in environmental damage cost of NH_3 associated with the use of Green UreaNV® and polymer-coated urea, when compared to urea (Table 1). We found the environmental damage cost (NH_3) avoided by using Green UreaNV® (AUD 46–137 ha^{-1}) would outweigh the additional cost of this fertilizer product (AUD 6.4 ha^{-1}) compared to urea. This results in net societal benefits of AUD 39–130 ha^{-1} (Table 1). While the damage cost of NH_3 loss has not been estimated for Australia, it is likely lower than that of the EU because of the lower NH_3 emission density and higher proportion of urban population in Australia than in the European countries, resulting in a stronger spatial disconnection between potentially exposed population and NH_3 emission sources (Crippa et al., 2018; Liang et al., 2018; Population Reference Bureau, 2018). Therefore, the lower bound of our estimates on societal benefits is more realistic for Australia. In contrast, when the environmental damage cost of NH_3 is low, the use of polymer-coated urea would not be cost-effective at the current market price in decreasing NH_3 loss (Table 1). Its cost-effectiveness will improve with the increase in the environmental damage cost of NH_3 (Table 1). This underpins the need of a cost-effective coating for controlled-release fertilizers.

In summary, we recommend that the environmental damage cost of N loss associated with fertilizer use should be considered when evaluating the mitigation potential of enhanced

efficiency fertilizers, and that this potential can be enhanced with the advancement in fertilizer technology. The potential societal benefits of enhanced efficiency fertilizers provide solid ground for subsidizing these products to compensate farmers for additional costs, particularly in regions with higher risk of NH_3 exposure of humans and ecosystems. This would promote the wider adoption of these products in agriculture for environmental sustainability.

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Figure captions

Fig. 1. Location of experimental site (Wye)

Fig. 2. Aerial layout of the experimental site for NH_3 measurement by two passive samplers mounted on a mast (■) at the three experimental areas fertilized with urea (blue circle), Green UreaNV® (green circle), and polymer-coated urea (red circle), and the background locations (not drawn to scale)

Fig. ~~1~~3. Cumulative ammonia (NH_3) volatilization from the application of urea, Green UreaNV®, and polymer-coated urea in the autumn (a) and spring (b) trials

Fig. ~~2~~4. Urea content in the soil under the treatment of urea, Green UreaNV®, and polymer-coated urea in the autumn (a) and spring (b) trials. Error bars represent standard errors of the mean of four replicates.

Fig. 5 NH_4^+ content in the soil under the treatment of urea, Green UreaNV®, and polymer-coated urea in the autumn (a) and spring (b) trials. Error bars represent standard errors of the mean of four replicates.

Tables

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Table 1

Extra fertilizer cost, reduction of NH_3 loss, and net benefits of using Green UreaNV® and polymer-coated urea, taking into consideration of the environmental damage cost of NH_3

	Urea (control)	Green UreaNV®	polymer-coated urea
Fertilizer cost (AUD t^{-1}) [a]	630	689	1500
Fertilizer N cost (AUD kg^{-1} N) [b]	1.37	1.50	3.26
Fertilizer application at 50 kg N ha^{-1}			
Fertilizer N cost at (AUD ha^{-1})	68.5	74.9	163.0
Extra fertilizer cost relative to urea (AUD ha^{-1}) (I)	--	6.4	94.6
Average cumulative NH_3 loss of the two trials (kg N ha^{-1})	5.7	2.85	1.1
Amount of NH_3 saved relative to urea (kg N ha^{-1})	--	2.85	4.6
Fertilizer N value of NH_3 saved relative to urea (AUD ha^{-1}) (II)	--	3.9	6.3
Benefit to farmers (AUD ha^{-1}) (II – I)		–2.5	–88.3
Amount of NH_3 damage cost avoided relative to urea (AUD ha^{-1}) (III)	--	46 to 137	74 to 221
Societal benefit relative to urea (AUD ha^{-1}) (III – I) [c]	--	39 to 130	–21 to 126

[a] Incitec Pivot Fertilisers port price list (effective February 2019)

[b] calculated based on the content of N in urea (46%)

[c] Environmental damage cost of NH_3, estimated to be € 10–30 per kg NH_3-N (van Grinsven et al., 2013; 2018), was converted into Australian dollars (AUD) 16–48 per kg NH_3-N based on exchange rate of AUD: Euro = 1.6:1.

Figure 1
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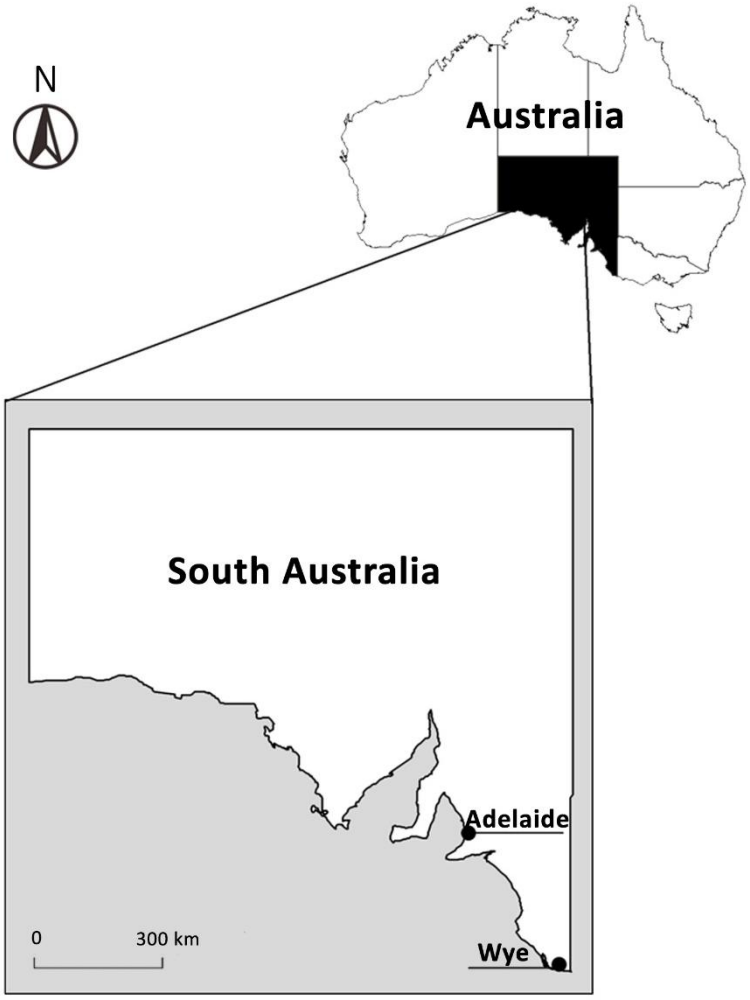


Fig. 1

Figure 2
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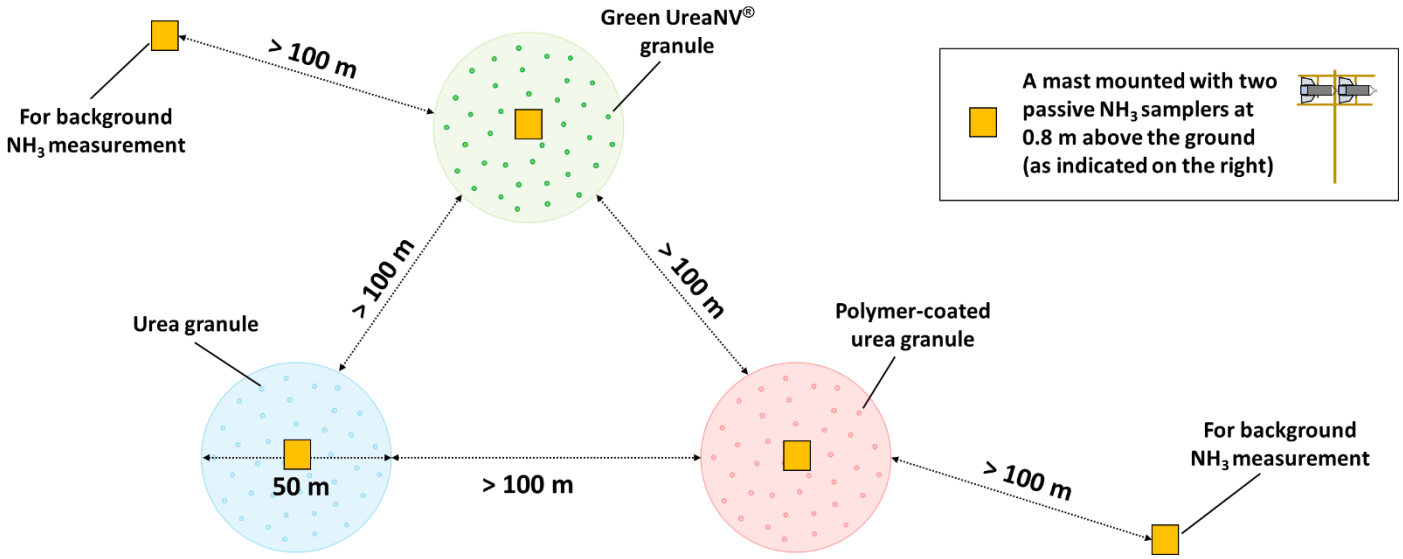


Fig. 2

Figure 3
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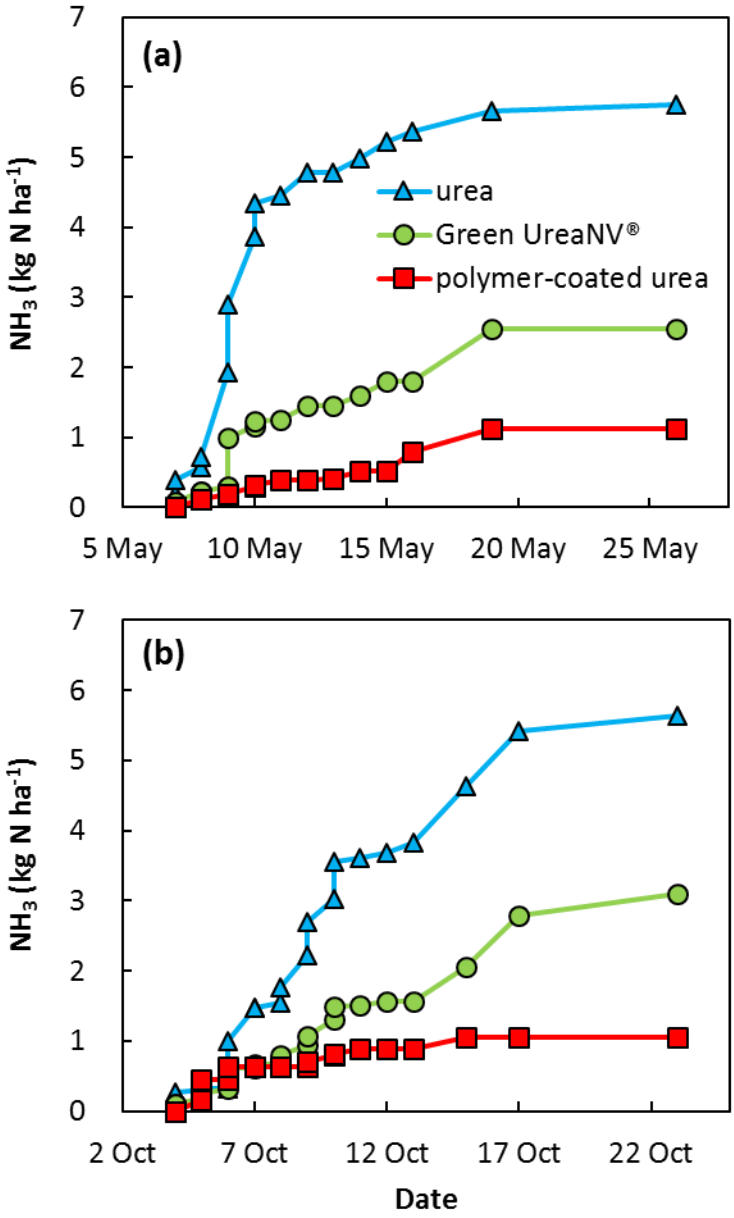


Fig. 3

Figure 4
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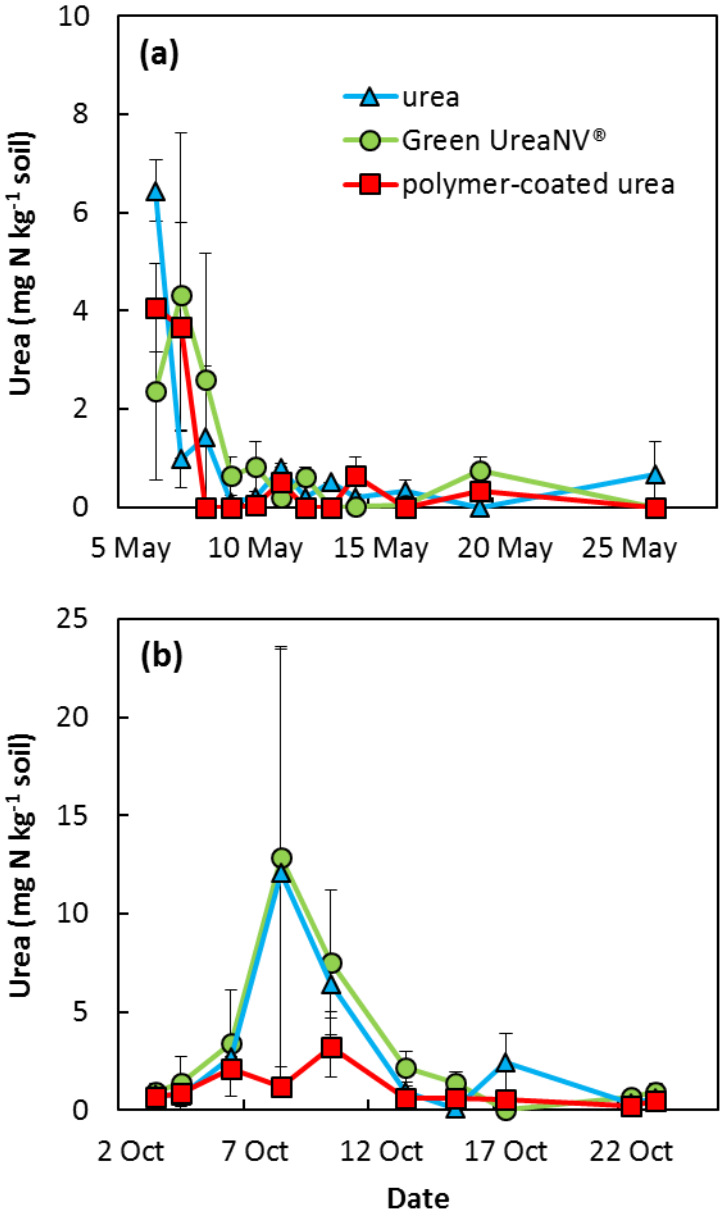


Fig. 4

Figure 5
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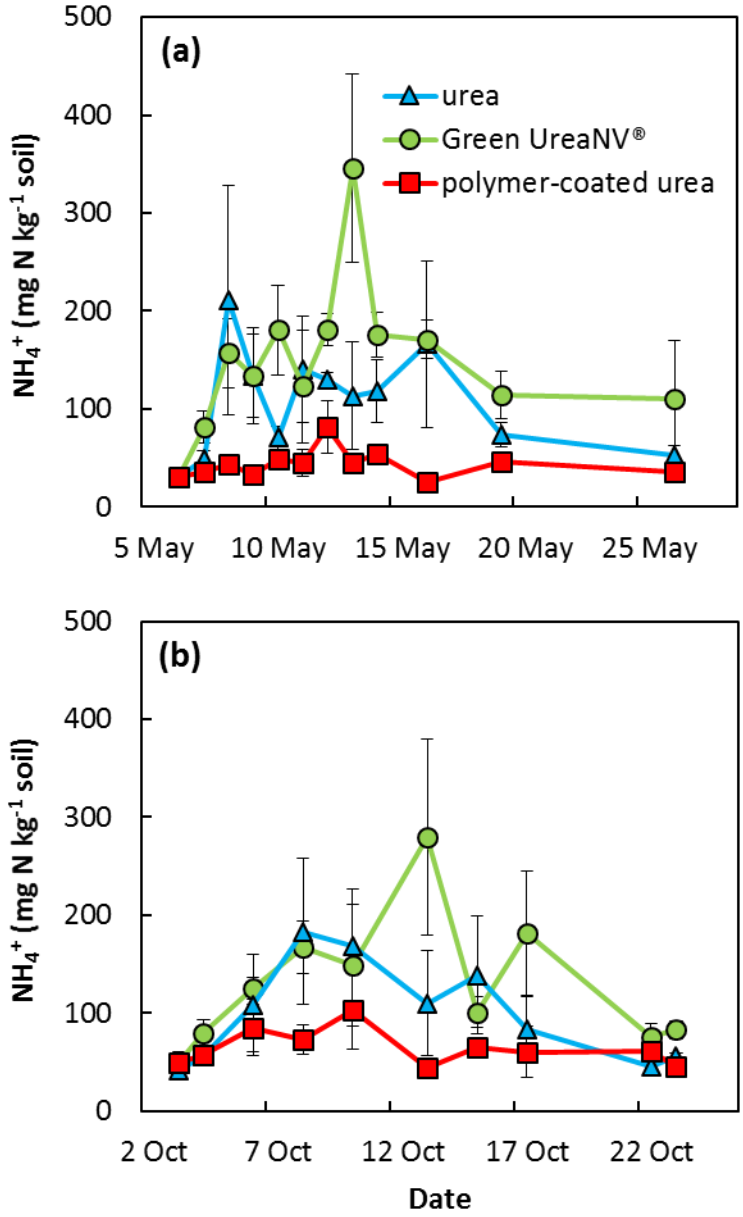


Fig. 5