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Title:

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

Date:

2019-11

Citation:

Lam, S. K., Suter, H., Bai, M., Walker, C., Mosier, A. R., van Grinsven, H. & Chen, D. (2019). Decreasing ammonia loss from an Australian pasture with the use of enhanced efficiency fertilizers. *Agriculture, Ecosystems & Environment*, 283 (November 2019), pp.106553-106553. <https://doi.org/10.1016/j.agee.2019.05.012>.

Persistent Link:

<https://hdl.handle.net/11343/299986>

1 **Title page**

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16

17 *Type of Paper*

18 Special issue VSI AgroEnviron 2018

19 **Abstract**

20 Mitigating ammonia (NH<sub>3</sub>) volatilization from intensive pasture systems is critical for  
21 environmental sustainability. However, field-scale evaluation on the potential of enhanced  
22 efficiency fertilizers (e.g. urease inhibitors and controlled-release fertilizers) in mitigating  
23 NH<sub>3</sub> volatilization is limited. Using a micrometeorological technique, we conducted two field  
24 trials to investigate the effects of Green UreaNV<sup>®</sup> (urea coated with the urease inhibitor *N*-(*n*-  
25 butyl)thiophosphoric triamide, NBPT) and polymer-coated urea (a controlled-release  
26 fertilizer) on NH<sub>3</sub> volatilization from an intensive rainfed pasture in southern Australia. We  
27 found that NH<sub>3</sub> volatilization from urea was 5.8 and 5.6 kg N ha<sup>-1</sup>, respectively, in the  
28 autumn and spring trials, equivalent to 11–12% of the applied urea in each season. The use of  
29 Green UreaNV<sup>®</sup> and polymer-coated urea decreased the cumulative NH<sub>3</sub> volatilization by  
30 45–55% and 80%, respectively. Taking into consideration the high environmental damage  
31 cost of NH<sub>3</sub> as found in the European Union, we hypothesize that both Green UreaNV<sup>®</sup> and  
32 polymer-coated urea can be cost-effective in mitigating NH<sub>3</sub> loss from this pasture. Our  
33 findings suggest that the extra cost of using these enhanced efficiency fertilizers for farmers  
34 is not compensated by the fertilizer N value of decreased NH<sub>3</sub> loss. However, from a societal  
35 perspective the extra cost for Green UreaNV<sup>®</sup> is likely outweighed by reduced environmental  
36 cost of NH<sub>3</sub>. New fertilizer technology should be developed to improve the cost-effectiveness  
37 of polymer-coated urea to the farmers.

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

40

41 **1. Introduction**

42 Ammonia (NH<sub>3</sub>) emission is conducive to the formation of fine secondary particulate matter  
43 (PM<sub>2.5</sub>) in the atmosphere (Schiferl et al., 2014; Wu et al., 2016). When deposited, NH<sub>3</sub> can

44 cause eutrophication of aquatic and terrestrial ecosystems, and nitrous oxide (N<sub>2</sub>O) emission  
45 (Mosier et al., 1998; Galloway et al., 2008). The adverse impact of agricultural NH<sub>3</sub>  
46 emissions on human health and ecosystems has been estimated at € 10–120 billion per year in  
47 the European Union (van Grinsven et al., 2013) and updated to € 40–120 billion per year  
48 taking into account improved evidence for health impacts of NH<sub>3</sub> aerosols and impacts on  
49 marine ecosystems (van Grinsven et al., 2018). This highlights the urgency of NH<sub>3</sub> mitigation.

50

51 Ammonia mitigation measures include the use of enhanced efficiency fertilizers such as urea  
52 granules coated with a urease inhibitor, and controlled-release fertilizers, which are proven to  
53 be effective when used in various agricultural systems (e.g. Pan et al., 2016; Xia et al., 2017).  
54 Urease inhibitors are compounds that inhibit urease activity, thereby allowing the urea to  
55 move into the soil before hydrolysis, and subsequently reduce NH<sub>3</sub> volatilization (Chen et al.,  
56 2008). Controlled-release fertilizers such as polymer-coated urea control the release of N  
57 from urea via the polymer coating which acts as a physical barrier, thus satisfying plant  
58 requirements while maintaining low mineral N availability in the soil (Chen et al., 2008).

59

60 Fertilizer N application in the Australian dairy industries increased rapidly from 21 kg N ha<sup>-1</sup>  
61 in 1990 to 94 kg N ha<sup>-1</sup> in 2012 (Stott and Gourley, 2016); urea is the most commonly used N  
62 fertilizer in pastures (Havilah et al., 2005). However, there are limited field-scale studies on  
63 the quantification of NH<sub>3</sub> volatilization from Australian dairy pastures (e.g. Prasertsak et al.,  
64 2001; Eckard et al., 2003; Denmead et al., 2004), and very few on the potential of enhanced  
65 efficiency fertilizers in mitigating this important pathway of N loss (Suter et al., 2013; Lam et  
66 al., 2018). This is likely because a reliable quantification of NH<sub>3</sub> volatilization at the field  
67 scale requires the use of micrometeorological techniques (Denmead, 1983; Cichota and Snow,  
68 2012), which involve huge labour and resource inputs, and large land area. In this study, we

69 conducted two field-scale measurements at a dairy pasture in a temperate region in southern  
70 Australia using a micrometeorological method. The objectives of the study were to  
71 investigate the effects of a urease inhibitor and a controlled-release coating on  $\text{NH}_3$   
72 volatilization from urea fertilizer in an intensive pasture system under open-air conditions,  
73 and to assess the economic and societal benefits of these enhanced efficiency fertilizers in  
74 mitigating  $\text{NH}_3$  volatilization.

75

## 76 **2. Materials and Methods**

### 77 *2.1 Experimental site*

78 Field experiments were conducted on a temperate pasture dominated by perennial ryegrass  
79 (*Lolium perenne*) at Wye (38°01' S, 140°53'E), South Australia, Australia (Fig. 1), in autumn  
80 (6–26 May 2014) and spring (3–23 October 2014). The average minimum and maximum  
81 temperatures during the experimental period in autumn were 10.0°C and 18.7°C, respectively,  
82 and 7.5°C and 21.2°C in spring. The rainfall during the same period was 28.6 mm and 12.8  
83 mm in autumn and spring, respectively (Bureau of Meteorology, 2013). A three-dimensional  
84 sonic anemometer (CSAT3, Campbell Scientific) was ~~established~~placed on the field site to  
85 measure wind speed and wind direction during the experimental period. The soil at the site is  
86 classified as a Tenosol (Isbell, 1996) with 78% sand, 18% silt and 4% clay. The surface soil  
87 (0–0.10 m) had a pH ( $\text{CaCl}_2$ ) of 4.9, and contained 4.9% organic C, 0.47% total N, 38.9 mg  
88  $\text{kg}^{-1}$   $\text{NH}_4^+$ -N and 28.8 mg  $\text{kg}^{-1}$   $\text{NO}_3^-$  at commencement of the experiment.

89

### 90 *2.2 Experimental design*

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

94 surface applied at a rate of 50 kg N ha<sup>-1</sup> on 6 May and 3 October to a 50 m diameter circular  
95 experimental area, with one circular area assigned to each treatment. The adjacent  
96 experimental areas were separated by at least 100 m to avoid cross-contamination of NH<sub>3</sub>  
97 [\(Fig. 2\)](#).

98

### 99 2.3 *NH<sub>3</sub> volatilization*

100 A micrometeorological mass-balance method was used to determine the NH<sub>3</sub> flux from each  
101 treatment (Freney et al., 1985). Two passive NH<sub>3</sub> samplers (Leuning et al., 1985) were placed  
102 at 0.8 m above the ground surface on a mast located at the centre of each experimental area  
103 [\(Fig. 2\)](#). This height of 0.8 m is denoted as ZINST, or the stability independent height, which  
104 allows satisfactory determination of NH<sub>3</sub> loss irrespective of the atmospheric stability  
105 (Wilson et al., 1982; Denmead, 1983).

106 Background measurements were made from the two sides of the experimental area along the  
107 dominant wind direction, using two masts with the same height as the treatment circles.

108 These masts were located at least 100 m from the edge of the closest circle [\(Fig. 2\)](#).

109 Following fertilizer application in the first week, NH<sub>3</sub> measurements were made twice daily  
110 during the periods 0800–1700 h and 1700–0800 h (overnight). When the NH<sub>3</sub> flux gradually  
111 decreased in the second week, measurements were made daily, and every two to three days  
112 when the flux declined further in the third week. For each measurement, NH<sub>3</sub> captured in the  
113 Leuning samplers was eluted with 40 mL MilliQ water and analyzed for NH<sub>4</sub><sup>+</sup>-N with a  
114 segmented flow analyzer (SAN<sup>++</sup>, Skalar) (Keeney and Nelson, 1982). Ammonia flux for  
115 each measurement period was calculated as described by Freney et al. (1985) and Leuning et  
116 al. (1985), and summed over time to compute the cumulative emission.

117

### 118 2.4 *Soil N*

119 Soil samples (0–5 cm) were collected with a 2.5-cm (internal diameter) auger from the  
120 circular treatment areas daily or every second day for a week after fertilizer application, then  
121 every second or third day for the second week, and once in the final week. For each quarter of  
122 the treatment circles 10 soil cores were sampled and composited. A subsample (10 g) was  
123 taken from the composited sample and kept frozen at  $-20^{\circ}\text{C}$  until extraction with 100 mL 2M  
124 KCl containing  $10\text{ mg L}^{-1}$  phenylmercuric acetate. The extract was filtered with Whatman No.  
125 42 filter papers and analyzed for urea and  $\text{NH}_4^+\text{-N}$  on the Skalar SAN<sup>++</sup> segmented flow  
126 analyzer.

127

### 128 2.5 Statistical analysis

129 Data of soil urea and  $\text{NH}_4^+$  contents were analyzed with MINITAB 16 statistical package  
130 using ANOVA. The least significant difference (l.s.d.) at  $p = 0.05$  was used to compare the  
131 means between the treatments (four replications). It was not possible to replicate  $\text{NH}_3$   
132 measurements owing to the large area required for each treatment ( $\sim 2,000\text{ m}^2$ ), which is  
133 common for large-scale  $\text{NH}_3$  flux measurements using the same micrometeorological  
134 technique (e.g. Turner et al., 2010). Nevertheless, this technique is robust for measurements  
135 of trace gas fluxes with uncertainty of within 15% (Denmead et al., 1998).

136

## 137 3. Results and discussion

### 138 3.1 Seasonal variation of ammonia volatilization

139 In the autumn trial,  $\text{NH}_3$  volatilization peaked three days after application of urea (9 May)  
140 and remained low ( $< 0.5\text{ kg N ha}^{-1}\text{ day}^{-1}$ ) thereafter for all treatments (Fig. 4a3a). In contrast,  
141  $\text{NH}_3$  volatilization in the spring trial was steady and lasted for around 12 days after urea  
142 application (Fig. 4b3b). Ammonia volatilization is dependent on edaphic and environmental  
143 factors such as soil pH, wind speed and soil moisture (Frenay et al., 1983). The volatilization

144 loss in our study site was driven by urea hydrolysis creating an alkaline hot spot (Du Preez  
145 and Burger, 1988) in this otherwise acidic environment (soil pH of 4.9). The average wind  
146 speed during the autumn and spring trials was 2.8 and 4.0 m s<sup>-1</sup>, respectively. This is  
147 desirable for NH<sub>3</sub> volatilization because wind blows NH<sub>3</sub>-rich air away from the soil surface  
148 and hence increases the NH<sub>3</sub> gradient between the air and the soil surface, and subsequently  
149 the rate of volatilization (Bolan et al., 2004).

150

151 In the autumn trial, the surface soil was sufficiently moistened by the heavy rainfall events  
152 (~50 mm on 3–5 May) before urea application on 6 May. The light rainfall events (1–2 mm)  
153 on 6 and 7 May allowed the urea granules to be dissolved but not diffused into the subsoil,  
154 resulting in an abrupt increase in NH<sub>3</sub> volatilization on 9 May (Fig. 4a3a). On 10 May the 7.6  
155 mm rainfall was sufficient to wash the urea down in the soil, and ~~since then~~after that low NH<sub>3</sub>  
156 emission was ~~noted~~measured. This is supported by the decline in urea content from 6 May to  
157 10 May (Fig. 2a4a). The effect of rainfall on NH<sub>3</sub> volatilization in our study is consistent with  
158 the findings by Sanz-Cobena et al. (2011), who found that low water input (3 mm rainfall)  
159 increased NH<sub>3</sub> emission but the emission became minimal when urea was washed into the  
160 subsoil by higher water input (7–14 mm rainfall).

161

162 In the spring trial, no rainfall events were recorded for four consecutive days prior to urea  
163 application on 3 October, rendering the surface soil dry, which delayed urea hydrolysis and  
164 NH<sub>3</sub> volatilization (Black et al., 1987). The light rainfall events on 6–8 October (3.6 mm) and  
165 13 October (2.6 mm) triggered NH<sub>3</sub> volatilization (Fig. 4b3b). During these rainfall events  
166 the urea granules were gradually dissolved, as indicated by the increase in urea content from  
167 6 October (Fig. 2b4b). Ammonia volatilization became minimal after the 6 mm rainfall on 16  
168 Oct, which likely washed all the urea down into the soil profile. The above results suggest

169 that rainfall events played an important role in NH<sub>3</sub> volatilization from this pasture, and that  
170 the timing of fertilizer application should be adjusted based on the likelihood of adequate  
171 rainfall events so as to minimize NH<sub>3</sub> volatilization.

172

### 173 *3.2 Mitigation of ammonia volatilization by enhanced efficiency fertilizers*

174 The cumulative NH<sub>3</sub> emission for the urea treatment was 5.8 and 5.6 kg N ha<sup>-1</sup> over the  
175 autumn and spring experimental periods, respectively, equivalent to 11–12% of the N applied.  
176 This percentage of N loss is comparable to the global average of 16% loss of N as NH<sub>3</sub> from  
177 surface applied urea in various agricultural systems (Pan et al., 2016). The N loss represents  
178 an economic loss to farmers of Australian dollars (AUD) 7.8 ha<sup>-1</sup> (5.7 kg N ha<sup>-1</sup> × 1.37 AUD  
179 kg<sup>-1</sup> N) (Table 1). More importantly, the potential damage cost of NH<sub>3</sub> to human health  
180 (particulate matter) and ecosystem (eutrophication, biodiversity) in the European Union has  
181 been estimated at € 10–30 per kg NH<sub>3</sub>-N (van Grinsven et al., 2013; 2018). Mitigation of  
182 NH<sub>3</sub> volatilization is therefore urgently needed to improve N use efficiency and  
183 environmental quality.

184

185 Ammonia volatilization can be decreased by adopting various mitigation strategies, as  
186 reported in recent global meta-analyses (Pan et al. 2016; Xia et al. 2017; Ti et al. 2019),  
187 including the use of urease inhibitors and controlled-release fertilizers. In our study, NH<sub>3</sub>  
188 emission in the autumn and spring trials was decreased by the Green UreaNV<sup>®</sup> (NBPT as the  
189 urease inhibitor) to 2.6 and 3.1 kg N ha<sup>-1</sup>, respectively, representing a 45–55% reduction (Fig.  
190 [43](#)). Likewise, the polymer-coated urea decreased NH<sub>3</sub> volatilization to 1.1 kg N ha<sup>-1</sup> in both  
191 trials, equivalent to an 80% reduction (Fig. [43](#)). The reduction induced by the urease inhibitor  
192 and the polymer-coated urea is similar to the ranges (53–54 and 57–68%, respectively)  
193 reported in the meta-analyses on NH<sub>3</sub> mitigation strategies (Pan et al., 2016; Ti et al., 2019).

194 The urease inhibitor NBPT inhibited urease activity and delayed urease hydrolysis (Sommer  
195 et al., 2004; Chen et al., 2008), thereby decreasing NH<sub>3</sub> volatilization. This is shown by the  
196 generally higher soil NH<sub>4</sub><sup>+</sup> content in the Green UreaNV<sup>®</sup> treatment than the urea treatment  
197 in both trials (Fig. 5a, b). ~~increase in~~The average soil NH<sub>4</sub><sup>+</sup> content increased from 107 (urea  
198 treatment) to 152 mg kg<sup>-1</sup> (Green UreaNV<sup>®</sup> treatment) in the autumn trial ( $p < 0.05$ ), and  
199 from 99 to 129 mg kg<sup>-1</sup> in spring ( $p < 0.05$ ). The relatively high soil NH<sub>4</sub><sup>+</sup> content (> 100 mg  
200 kg<sup>-1</sup>) in this pasture was likely because NH<sub>4</sub><sup>+</sup> was retained in the soil, rather than being  
201 volatilized, in this acidic soil environment, combined with the relatively high background N  
202 due to past management of the pasture site. The polymer-coated urea, as a controlled-release  
203 fertilizer, slowed ~~down~~ urea release from the fertilizer granules (Chen et al., 2008).  
204 Consequently, throughout the experimental period, the NH<sub>4</sub><sup>+</sup> content under the treatment of  
205 polymer-coated urea (averaging 44 and 64 mg kg<sup>-1</sup> in autumn and spring, respectively) was  
206 much lower than the urea treatment ( $p < 0.05$ ) (Fig. 5a, b), and NH<sub>3</sub> volatilization was also  
207 decreased.

208

209 It is worth noting that fertilizers with urease inhibitor and controlled-release coatings are not  
210 widely adopted despite their effectiveness in mitigating NH<sub>3</sub> volatilization from various  
211 agricultural systems globally. One major obstacle preventing the wider adoption is that the  
212 extra cost of these fertilizer products (Table 1) may not secure productivity benefits (e.g.  
213 Suter et al., 2013; Nauer et al., 2018), as also observed in this field site (Suter et al.,  
214 unpublished). This lack of productivity response in pastures has been attributed to non-  
215 limiting background soil N, unfavourable climatic conditions and differential responses of  
216 pasture species (Suter et al. 2013; Di and Cameron, 2016). We found that there were no  
217 financial benefits to farmers because the fertilizer N value of NH<sub>3</sub> saved by using Green  
218 UreaNV<sup>®</sup> and polymer-coated urea was lower than the extra cost of these products (Table 1).

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

221

222 | Nonetheless, a far more important but often ignored concern is the environmental  
223 | sustainability of the system. As mentioned, the estimated environmental damage cost of NH<sub>3</sub>  
224 | is € 10–30 per kg NH<sub>3</sub>-N (van Grinsven et al., 2013). We performed a simple economic  
225 | assessment for this Australian pasture based on the increase in fertilizer cost and the decrease  
226 | in environmental damage cost of NH<sub>3</sub> associated with the use of Green UreaNV<sup>®</sup> and  
227 | polymer-coated urea, when compared to urea (Table 1). We found the environmental damage  
228 | cost (NH<sub>3</sub>) avoided by using Green UreaNV<sup>®</sup> (AUD 46–137 ha<sup>-1</sup>) would outweigh the  
229 | additional cost of this fertilizer product (AUD 6.4 ha<sup>-1</sup>) compared to urea. This results in net  
230 | societal benefits of AUD 39–130 ha<sup>-1</sup> (Table 1). While the damage cost of NH<sub>3</sub> loss has not  
231 | been estimated for Australia, it is likely lower than that of the EU because of the lower NH<sub>3</sub>  
232 | emission density and higher proportion of urban population in Australia than in the European  
233 | countries, resulting in a stronger spatial disconnection between potentially exposed  
234 | population and NH<sub>3</sub> emission sources (Crippa et al., 2018; Liang et al., 2018; Population  
235 | Reference Bureau, 2018). Therefore, the lower bound of our estimates on societal benefits is  
236 | more realistic for Australia. In contrast, when the environmental damage cost of NH<sub>3</sub> is low,  
237 | the use of polymer-coated urea would not be cost-effective at the current market price in  
238 | decreasing NH<sub>3</sub> loss (Table 1). Its cost-effectiveness will improve with the increase in the  
239 | environmental damage cost of NH<sub>3</sub> (Table 1). This underpins the need of a cost-effective  
240 | coating for controlled-release fertilizers.

241

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

244 efficiency fertilizers, and that this potential can be enhanced with the advancement in  
245 fertilizer technology. The potential societal benefits of enhanced efficiency fertilizers provide  
246 solid ground for subsidizing these products to compensate farmers for additional costs,  
247 particularly in regions with higher risk of NH<sub>3</sub> exposure of humans and ecosystems. This  
248 would promote the wider adoption of these products in agriculture for environmental  
249 sustainability.

250

### 251 **Acknowledgements**

252 This research was undertaken as part of the National Agricultural Nitrous Oxide Research  
253 Program funded by the Australian Department of Agriculture and Incitec Pivot Fertilisers.  
254 The authors acknowledge support from Australian Research Council Linkage Project  
255 (LP160101417). The authors thank Rick Jordan for site access and assistance in site selection,  
256 Dr. Hang-wei Hu, Dr. Rui Liu, Dr. Trevor Coates, Miss Sima Mazaheri and Mr. Eric Ireland  
257 for field assistance and soil chemical analyses.

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366

367 **Figure captions**

368 **Fig. 1.** Location of experimental site (Wye)

369

370 **Fig. 2.** Aerial layout of the experimental site for NH<sub>3</sub> measurement by two passive  
371 samplers mounted on a mast (■) at the three experimental areas fertilized  
372 with urea (blue circle), Green UreaNV<sup>®</sup> (green circle), and polymer-coated  
373 urea (red circle), and the background locations (not drawn to scale)

374

375 **Fig. 13.** Cumulative ammonia (NH<sub>3</sub>) volatilization from the application of urea, Green  
376 UreaNV<sup>®</sup>, and polymer-coated urea in the autumn (a) and spring (b) trials

377

378 **Fig. 24.** Urea content in the soil under the treatment of urea, Green UreaNV<sup>®</sup>, and  
379 polymer-coated urea in the autumn (a) and spring (b) trials. Error bars represent standard  
380 errors of the mean of four replicates.

381

382 **Fig. 5** NH<sub>4</sub><sup>+</sup> content in the soil under the treatment of urea, Green UreaNV<sup>®</sup>, and  
383 polymer-coated urea in the autumn (a) and spring (b) trials. Error bars represent standard  
384 errors of the mean of four replicates.

**Table 1**

Extra fertilizer cost, reduction of NH<sub>3</sub> loss, and net benefits of using Green UreaNV<sup>®</sup> and polymer-coated urea, taking into consideration of the environmental damage cost of NH<sub>3</sub>

	Urea (control)	Green UreaNV <sup>®</sup>	polymer- coated urea
Fertilizer cost (AUD t <sup>-1</sup> ) <sup>a</sup>	630	689	1500
Fertilizer N cost (AUD kg <sup>-1</sup> N) <sup>b</sup>	1.37	1.50	3.26
<u>Fertilizer application at 50 kg N ha<sup>-1</sup></u>			
Fertilizer N cost at (AUD ha <sup>-1</sup> )	68.5	74.9	163.0
Extra fertilizer cost relative to urea (AUD ha <sup>-1</sup> ) (I)	--	6.4	94.6
Average cumulative NH <sub>3</sub> loss of the two trials (kg N ha <sup>-1</sup> )	5.7	2.85	1.1
Amount of NH <sub>3</sub> saved relative to urea (kg N ha <sup>-1</sup> )	--	2.85	4.6
Fertilizer N value of NH <sub>3</sub> saved relative to urea (AUD ha <sup>-1</sup> ) (II)	--	3.9	6.3
Benefit to farmers (AUD ha <sup>-1</sup> ) (II – I)		-2.5	-88.3
Amount of NH <sub>3</sub> damage cost avoided relative to urea (AUD ha <sup>-1</sup> ) (III)	--	46 to 137	74 to 221
Societal benefit relative to urea (AUD ha <sup>-1</sup> ) (III – I) <sup>c</sup>	--	39 to 130	-21 to 126

<sup>a</sup> Incitec Pivot Fertilisers port price list (effective February 2019)

<sup>b</sup> calculated based on the content of N in urea (46%)

<sup>c</sup> Environmental damage cost of NH<sub>3</sub>, estimated to be € 10–30 per kg NH<sub>3</sub>-N (van Grinsven et al., 2013; 2018), was converted into Australian dollars (AUD) 16–48 per kg NH<sub>3</sub>-N based on exchange rate of AUD: Euro = 1.6:1.



**Fig. 1**

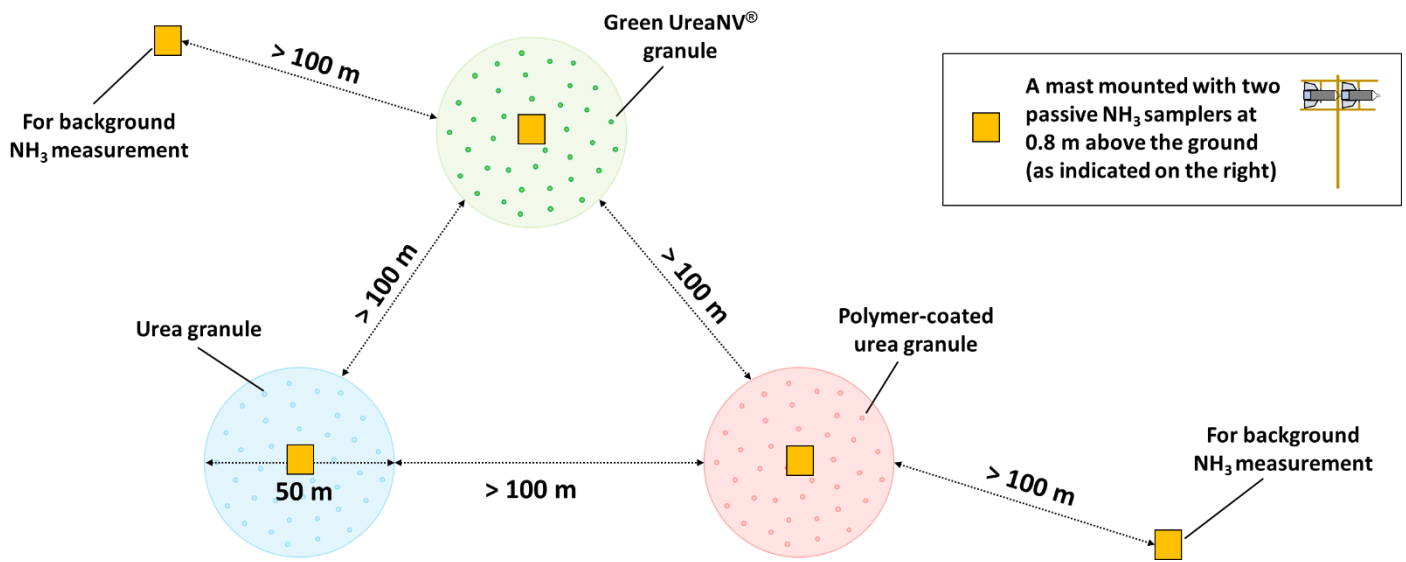


Fig. 2

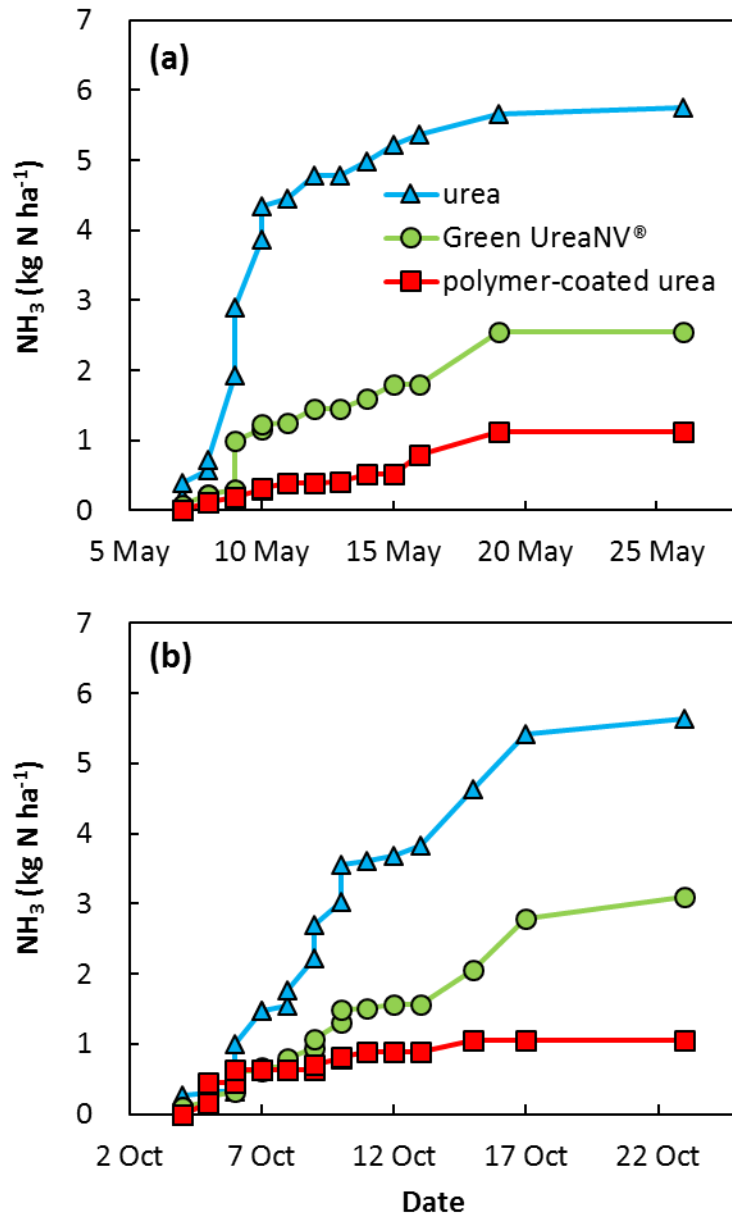


Fig. 3

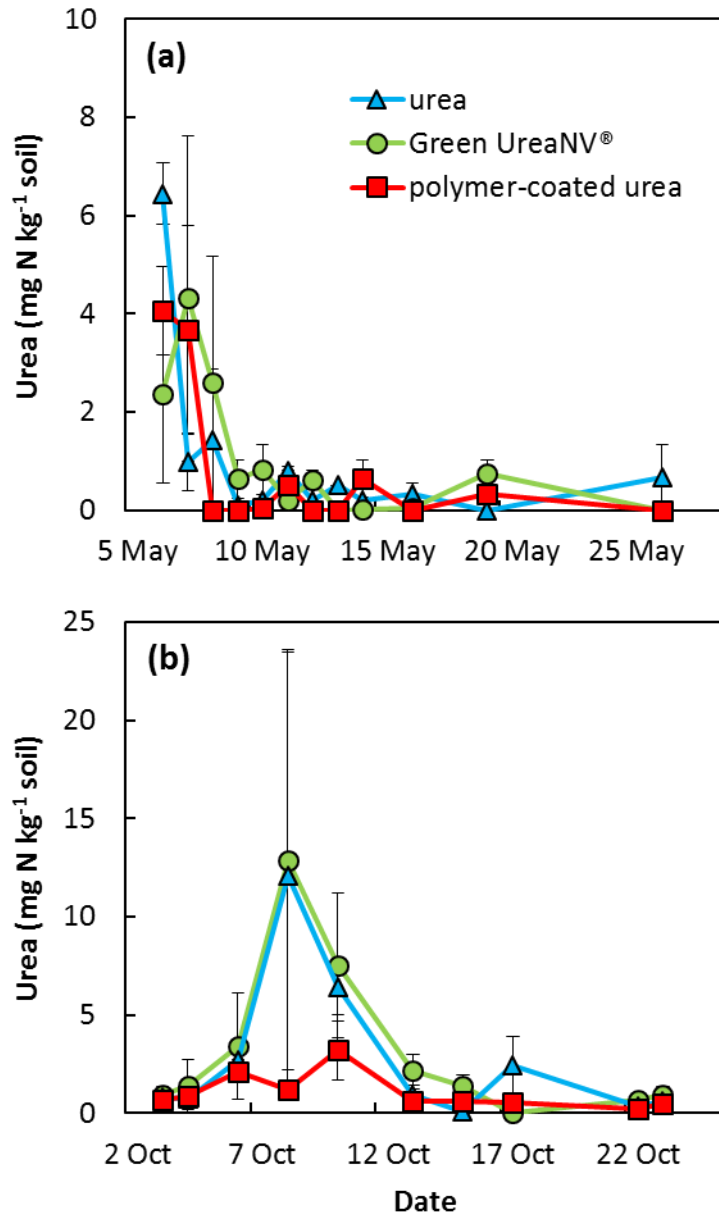


Fig. 4

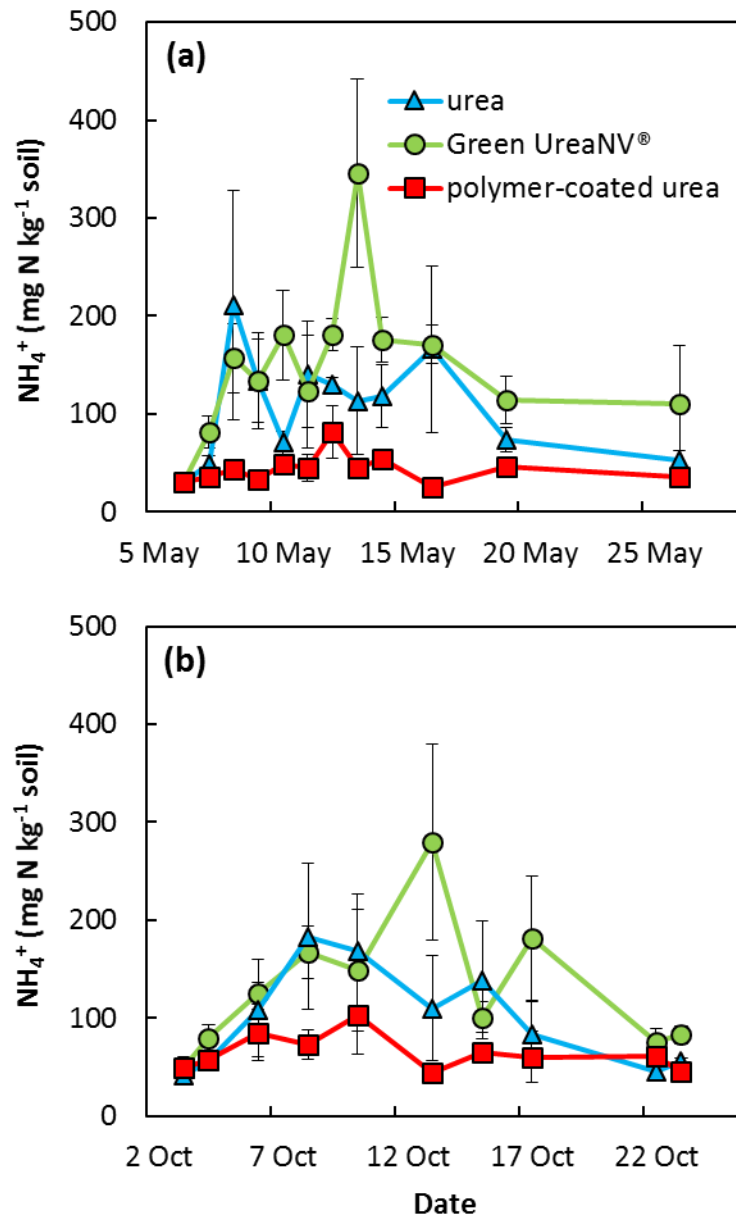


Fig. 5