Dual effects of nitrification inhibitors on agricultural N$_2$O emission

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Abstract
Nitrification inhibitors are effective in decreasing nitrous oxide (N$_2$O) emission from agricultural systems worldwide, but can increase ammonia (NH$_3$) volatilization and subsequently, indirect N$_2$O emission. This is often neglected when evaluating the inhibitors as a climate change mitigation tool. In our recent literature review, we found that when the indirect N$_2$O emission from deposited NH$_3$ was considered, the overall impact of nitrification inhibitors ranged from –4.5 to +0.5 kg N$_2$O-N ha^{-1}. We noted that no such experiment was reported in the literature for vegetable production systems, which have high risk of NH$_3$ and N$_2$O loss from high N input (as manures and synthetic fertilizers) and high water input. We therefore conducted a case study field experiment to simultaneously quantify the effect a nitrification inhibitor, 3,4-dimethylpyrazole phosphate (DMPP) on NH$_3$ and N$_2$O emissions from surface applied chicken manure and synthetic fertilizers in a vegetable production system using a micrometeorological approach. The cumulative NH$_3$ emissions over the measurement period were 19.7 and 27.0 kg N ha^{-1} for the control and DMPP treatment (an increase of 7.3 kg N ha^{-1}, or 37% with DMPP). The corresponding values for the cumulative direct N$_2$O emission over the measurement period were 6.0 and 3.8 kg N ha^{-1} (a decrease of 2.3 kg N ha^{-1}, or 38% with DMPP). This suggests that the beneficial effect of nitrification inhibitors in decreasing direct N$_2$O emission may be undermined by the concomitant increase in NH$_3$ volatilization.

Key words
Nitrification inhibitor, 3,4-dimethyl pyrazole phosphate, nitrous oxide, ammonia, vegetable production system, open-path Fourier Transform Infrared spectroscopy, micrometeorological technique

Introduction
Globally, agriculture contributes about 60% of total anthropogenic emission of nitrous oxide (N$_2$O), a potent greenhouse gas (GHG) (Ciais *et al*. 2013). Nitrification inhibitors temporarily suppress the microbial conversion of ammonium (NH$_4^+$) to nitrite (NO$_2^-$) in soil and have been extensively investigated for their ability to decrease N$_2$O emissions across a broad range of agricultural systems (Chen *et al*. 2008; Qiao *et al*. 2015).

The use of nitrification inhibitors, however, prolongs the retention of NH$_4^+$ in soil, which could potentially increase ammonia (NH$_3$) emission (Zaman and Nguyen 2012). Deposition of emitted NH$_3$ poses a major threat to environmental quality and ecosystem biodiversity e.g. through eutrophication (Erisman *et al*. 2008), and indirectly contributes to N$_2$O emission (van der Gon and Bleeker 2005) through subsequent nitrification and denitrification processes. According to the IPCC guidelines (De Klein *et al*. 2006), about 1% of the NH$_3$ emitted is converted to N$_2$O after deposition to land. The inclusion of indirect N$_2$O emission is critical to evaluating the effectiveness of nitrification inhibitors in mitigating GHG emissions from agriculture. Recently, Lam *et al*. (2016) reviewed studies that simultaneously measure both N$_2$O and NH$_3$ emissions in the field and quantified the overall effect of nitrification inhibitors on N$_2$O and NH$_3$ emission. The authors found that nitrification inhibitors decreased direct N$_2$O emission by 0.2–4.5 kg N$_2$O-N ha^{-1} (8–57%), but generally increased NH$_3$ emission, by 0.2–18.7 kg NH$_3$-N ha^{-1} (3–65%). Taking into account the estimated indirect N$_2$O emission from deposited NH$_3$, the overall impact of nitrification inhibitors ranged from –4.5 (reduction) to +0.5 (increase) kg N$_2$O-N ha^{-1}.

There has been no previous published measurement of the net impact of nitrification inhibitors on N$_2$O emissions for vegetable production systems, which have high risk of NH$_3$ and N$_2$O loss from high N input (as manures and synthetic fertilizers) (up to 1000 kg N ha^{-1}, Chen *et al*. 2014), high water input, but low N use efficiency (as low as < 10%, Zhu *et al*. 2005). We also observed that the closed-chamber (CC) method was used in most studies for measuring N$_2$O emissions and the open-chamber (OC) method for NH$_3$ volatilization (Lam *et al*. 2016). Whilst these techniques may be suitable at the small scale, the high

heterogeneity of emissions from agricultural systems lends itself to use of micrometeorological techniques to obtain continuous, non-intrusive and paddock-scale gas measurements.

We therefore conducted a case study field experiment to simultaneously quantify the effect of a nitrification inhibitor, 3,4-dimethylpyrazole phosphate (DMPP) on NH_3 and N_2O emissions from surface applied chicken manure and synthetic fertilizers in a vegetable production system using a micrometeorological approach.

Methods
The vegetable trial was conducted at Boneo (38.4°S, 144.9°E), Victoria, Australia, at the same site as reported in Lam *et al*. (2015). Celery (*Apium graveolens*) plants were transplanted on 6 and 7 April 2013 at the 4–5-leaf stage and received post-transplant fertilizer (calcium nitrate) at 39 kg N ha^{-1} five days after. The gas measurement was conducted between 1 and 24 May. Chicken manure (3.4% N) was transported and surface applied to the celery growing beds at 255 kg N ha^{-1} on 6 and 7 May and Nitrophoska® (12% N) at 39 kg N ha^{-1} on 14 May. The average minimum and maximum temperatures during the study period were 7.7°C and 17.4°C, respectively, with a total rainfall of 108 mm (Bureau of Meteorology 2013) and irrigation of 96 mm. Two paddocks (243 m × 192 m) were used for this study, one for the control (standard practice) and the other for the treatment with DMPP (applied at 6.6 kg ha^{-1} to the paddock on 8 May after manure application). The soil is classified as a Tenosol (Isbell 1996) with 91% sand. The soil (0–15 cm) has a pH (1:5 soil: water) of 7.9 and contains 0.64% organic carbon. Topsoil mineral N concentrations did not differ between the two paddocks, and ranged from 15.7–16.1 mg NH_4^+-N kg^{-1} and 11.4–11.7 mg NO_3^--N kg^{-1} five days after the celery transplant.

Details of the micrometeorological gas measurement technique of open-path Fourier transform infrared (OP-FTIR) spectroscopy in conjunction with the WindTrax model have been described in Bai *et al*. (2014). Briefly, an OP-FTIR spectroscopic system (Matrix-M IRcube, Bruker Optik GmbH) was established at the centre of each paddock at 1.2 m height with a path length of 98 m. Ammonia and N_2O concentrations were continuously measured at 3-min intervals. Measured spectra were analyzed at spectral regions of 900 cm^{-1} and 2300 cm^{-1} for NH_3 and N_2O, respectively. A three-dimensional sonic anemometer (CSAT3, Campbell Scientific) was located at the centre of each paddock at 2.3 m height. Ten-minute averaged micrometeorological data including wind speed, wind direction, air temperature, pressure and wind turbulent statistics were recorded at 10 Hz. The fluxes of NH_3 and N_2O were calculated at 10-min intervals using the *backward Lagrangian stochastic* (bLS) model (WindTrax 2.0, Thunder Beach Scientific).

Results and Discussion
Ammonia volatilization was negligible prior to manure application, but increased rapidly during the transportation and spreading of manure (on 6 and 7 May) (Figure 1). The pHs of the soil and the manure were 7.9 and 7.4, respectively, which was favourable for NH_3 volatilization (Freney *et al*. 1983). The cumulative NH_3 emissions over the measurement period were 19.7 and 27.0 kg N ha^{-1}, respectively for the control and DMPP treatment (an increase of 7.3 kg N ha^{-1}, or 37% with DMPP), accounting for 8% and 11% of the manure N applied. Around 98% (19.5 and 26.4 kg N ha^{-1} for the control and DMPP treatment, respectively) of the total NH_3 emission from each treatment occurred within the first week following manure application (Figure 1). We also observed 7% higher topsoil NH_4^+ concentration in the DMPP treatment (32.1 mg N kg^{-1}) than the control (29.9 mg N kg^{-1}) when averaged across the measurement period Ammonia volatilization associated with the application of synthetic fertilizer was small. This was attributed to the lower application rate compared to that of manure, and the irrigation event that washed the fertilizer N into the soil.

Our previous work (Lam *et al*. 2015) indicated that DMPP significantly decreased topsoil NO_3^- concentration and direct N_2O emission (measured by both OP-FTIR and chamber techniques) from this vegetable farm by 49% and 38%, respectively. The cumulative direct N_2O emissions over the measurement period were 6.0 and 3.8 kg N ha^{-1}, respectively for the control and DMPP treatment (a decrease of 2.3 kg N ha^{-1}, or 38% with DMPP) (Table 1). Based on the IPCC default EF$_4$ of 1% (mean) and 5% (upper range), we estimated that the overall effect of DMPP on N_2O emission (direct and indirect) was a decrease by 1.9–2.2 kg N_2O-N ha^{-1} (Table 1). This is within the range of observed impacts in other agroecosystems (Lam *et al*. 2016).
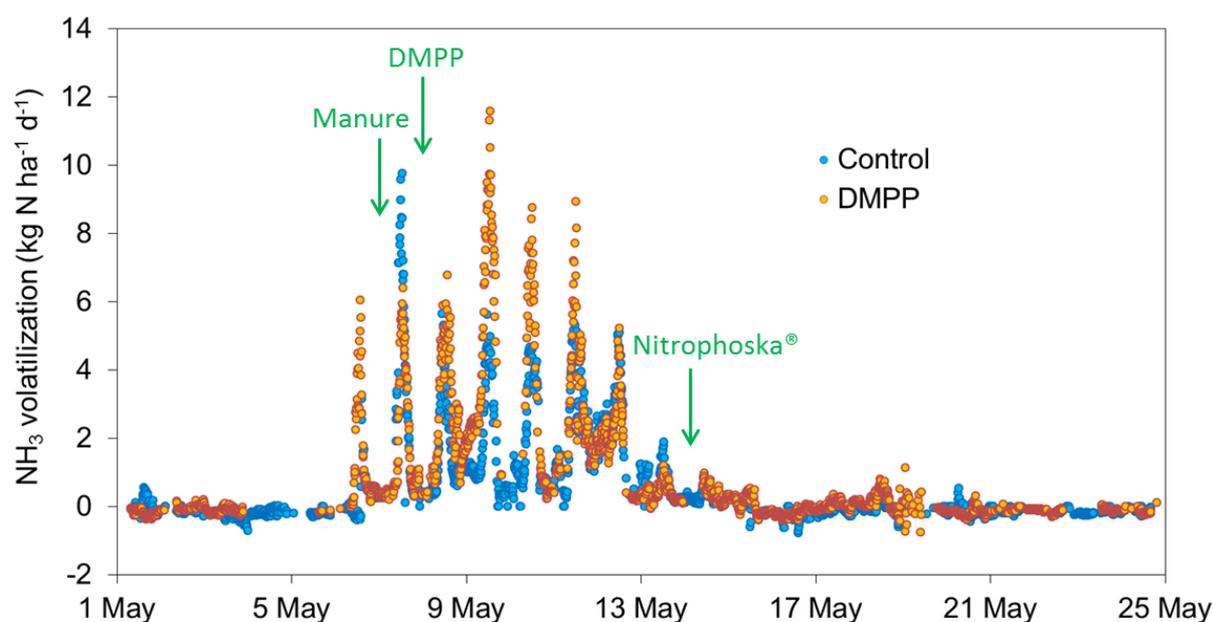
Figure 1. Effect of the nitrification inhibitor DMPP application on NH₃ volatilization measured by OP-FTIR spectroscopy. DMPP: 3,4-dimethylpyrazole phosphate. Green arrows represent the timing of applications of manure, DMPP and Nitrophoska®.

Table 1. Effect of DMPP on N₂O and NH₃ emissions from the case study site measured by OP-FTIR spectroscopy

	Effect of nitrification inhibitor (NI)			
	Direct N$_2$O emission (kg N ha^{-1})		NH$_3$ volatilization (kg N ha^{-1})	
	control	DMPP	control	DMPP
	6.04	3.75	19.72	26.99
% change	−37.9		+36.9	
Absolute change (kg N ha^{-1})	−2.29 (I)		+7.27 (II)	
Overall DMPP effect on N$_2$O emission (kg N ha^{-1})	I + II × EF$_4$ [a]			
EF$_4$ = 1%	−2.22			
EF$_4$ = 5%	−1.93			

[a] EF$_4$ of 1% and 5% represent the mean and upper range, respectively, of the IPCC default emission factor for indirect N$_2$O emission (De Klein et al. 2006)

The results of our literature review (Lam *et al*. 2016) and the current study (Table 1) indicate that nitrification inhibitors effectively decrease direct N₂O emission from agricultural systems. Nonetheless, this beneficial effect can be attenuated (this study), or reverted (Lam *et al*. 2016), by the estimated concomitant increase in indirect N₂O emission from deposited NH₃. This highlights the importance of considering both gases when evaluating the use of nitrification inhibitors as a climate change mitigation option.

References

Bai M, Suter H, Lam SK, Sun J, Chen D (2014) Use of open-path FTIR and inverse dispersion technique to quantify gaseous nitrogen loss from an intensive vegetable production site. Atmospheric Environment, 94, 687-691.

Bureau of Meteorology (2013) Climate Data Online http://www.bom.gov.au/climate/data/index.shtml Viewed 18 July 2014.

Chen D, Suter H, Islam A, Edis R, Freney JR, Walker CN (2008) Prospects of improving efficiency of fertilizer nitrogen in Australian agriculture: a review of enhanced efficiency fertilizers. Australian Journal of Soil Research, 46, 289-301.

Chen Q, Zhang XS, Zhang HY, Christie P, Li XL, Horlacher D, Liebig HP (2004) Evaluation of current fertilizer practice and soil fertility in vegetable production in the Beijing region. Nutrient Cycling in Agroecosytems, 69, 51-58.

Ciais P, Sabine C, Bala G et al. (Eds) (2013) Carbon and Other Biogeochemical Cycles. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

De Klein C, Novoa RSA, Ogle S et al. (2006) N_2O emissions from managed soils, and CO_2 emissions from lime and urea application. In: IPCC Guidelines for National Greenhouse Gas Inventories (Eds Eggleston HS, Buendia L, Miwa K, Ngara T, Tanabe K). Hayama, Japan, IGES.

Erisman JW, Sutton MA, Galloway J, Klimont Z, Winiwarter W (2008) How a century of ammonia synthesis changed the world. Nature Geoscience, 1, 636-639.

Freney JR, Simpson JR, Denmead OT (1983) Volatilization of ammonia. In: Gaseous loss of nitrogen from plant-soil systems (Eds Freney JR, Simpson JR), The Hague, Boston; Martinus Nijhoff Publishers, Hingham.

Isbell RF (1996) The Australian Soil Classification. Australian Soil and Land Survey Handbook, Melbourne, CSIRO Publishing.

Lam SK, Suter H, Davies R, Bai M, Sun J, Chen D (2015) Measurement and mitigation of nitrous oxide emissions from a high nitrogen input vegetable system. Scientific Reports, 5, 8208.

Lam SK, Suter H, Mosier AR, Chen D (2016) Using nitrification inhibitors to mitigate agricultural N_2O emission: a double-edged sword? Global Change Biology, DOI: 10.1111/gcb.13338.

Qiao C, Liu L, Hu S, Compton JE, Greaver TL, Li Q (2015) How inhibiting nitrification affects nitrogen cycle and reduces environmental impacts of anthropogenic nitrogen input. Global Change Biology, 21, 1249–1257.

Van Der Gon HD, Bleeker A (2005) Indirect N_2O emission due to atmospheric N deposition for the Netherlands. Atmospheric Environment, 39, 5827-5838.

Zaman M, Nguyen ML (2012) How application timings of urease and nitrification inhibitors affect N losses from urine patches in pastoral system. Agriculture, Ecosystems & Environment, 156, 37-48.