Measurement and mitigation of nitrous oxide emissions from a high nitrogen input vegetable system

Shu Kee Lam¹, Helen Suter¹, Rohan Davies², Mei Bai¹, Jianlei Sun¹ & Deli Chen¹

¹Crop and Soil Science Section, Faculty of Veterinary and Agricultural Sciences, The University of Melbourne, Victoria 3010, Australia; ²BASF Australia Ltd., Level 12, 28 Freshwater Place, Southbank, Victoria 3006, Australia.

The emission and mitigation of nitrous oxide (N₂O) from high nitrogen (N) vegetable systems is not well understood. Nitrification inhibitors are widely used to decrease N₂O emissions in many cropping systems. However, most N₂O flux measurements and inhibitor impacts have been made with small chambers and have not been investigated at a paddock-scale using micrometeorological techniques. We quantified N₂O fluxes over a four ha celery paddock using open-path Fourier Transform Infrared spectroscopy in conjunction with a backward Lagrangian stochastic model, in addition to using a closed chamber technique. The celery crop was grown on a sandy soil in southern Victoria, Australia. The emission of N₂O was measured following the application of chicken manure and N fertilizer with and without the application of a nitrification inhibitor 3, 4-dimethyl pyrazole phosphate (DMPP). The two techniques consistently demonstrated that DMPP application reduced N₂O emission by 37–44%, even though the N₂O fluxes measured by a micrometeorological technique were more than 10 times higher than the small chamber measurements. The results suggest that nitrification inhibitors have the potential to mitigate N₂O emission from intensive vegetable production systems, and that the national soil N₂O emission inventory assessments and modelling predictions may vary with gas measurement techniques.

Globally, agriculture contributes about 58% of total anthropogenic emissions of nitrous oxide (N₂O), a greenhouse gas 300 times more potent than carbon dioxide¹. Irrigated vegetable production systems use large nitrogen (N) input which can be susceptible to substantial N loss, including N₂O emission². The recovery of the applied N by vegetable crops rarely exceeds 50% and can be as low as 20%³. Nitrification inhibitors inhibit nitrification and subsequent denitrification, thereby reducing N₂O production⁴. A global meta-analysis suggests that nitrification inhibitors reduce N₂O emissions by 31–44% in agricultural systems⁵. Nevertheless, there is a dearth of information on the effect of nitrification inhibitors on N₂O emission from intensive vegetable production systems, and large-scale measurements with the use of a micrometeorological technique have not been conducted. This information is needed for efficient N management and mitigation of agricultural greenhouse gas emission. We therefore conducted a field experiment to investigate the effect of a nitrification inhibitor 3, 4-dimethylpyrazole phosphate (DMPP) on N₂O emission from a vegetable farm in Boneo (38.4°S, 144.9°E) Victoria, Australia. In addition to the widely used closed chamber method, we quantified paddock-scale N₂O fluxes with and without DMPP application using an open-path Fourier Transform Infrared spectroscopy (FTIR) in conjunction with a backward Lagrangian stochastic (bLS) model⁶.

Results and Discussion

Nitrous oxide emission from the celery paddocks increased after the application of chicken manure and Nitrophoska® regardless of DMPP treatment (Fig. 1). The emission was mostly from the celery growing bed where N was applied rather than from the furrow (Fig. 1b). The meteorological and chamber techniques showed that the application of DMPP reduced the N₂O emission by 37–44% (Table 1). The percentage decrease in N₂O emission in our study was comparable to that reported in ref. 7, which showed a 40–45% reduction of N₂O emission (from closed chambers) in a DMPP-treated lettuce-cauliflower farm in Germany. In contrast, a 75% decrease in the emission (from automatic chambers) was noted when DMPP was applied to a broccoli farm in subtropical Australia⁸. The actual N₂O emission from this broccoli farm was lower than that observed in our study and in ref. 7. Our study and that of ref. 7 were conducted in temperate regions while that of ref. 8 in a subtropical...
The difference in the effectiveness of DMPP in lowering N$_2$O production between these studies could be attributed to the actual N$_2$O emission and environmental factors such as soil temperature and moisture content, which may affect soil microbial metabolism and/or populations.

A nitrification inhibitor lowers N$_2$O emission by preventing or slowing the microbial conversion of ammonium (NH$_4^+$) to nitrate (NO$_3^-$) (ref. 4, 10). In our study, soil NO$_3^-$ content in the DMPP-treated celery growing bed was decreased by an average of 49% ($p < 0.001$) (Fig. 2b), which explains why N$_2$O emission was lower under DMPP application. The decrease in soil NO$_3^-$ content also suggests that NO$_3^-$ leaching was likely reduced in the paddock treated with DMPP. Soil NH$_4^+$ content did not differ significantly between the control and DMPP treatment (Fig. 2a). Nonetheless, any DMPP-induced difference in NH$_4^+$ content in our study would be small when compared to the substantial NH$_3$ volatilisation resulting from the high rate of surface NH$_4^+$-N application and alkaline soil pH$^{12,13}$.

The relative effects of DMPP on N$_2$O fluxes were consistent between the two techniques used in our study, despite the absolute flux values measured by these techniques differing by 7- to 40-fold under different background N$_2$O enhancement concentrations (Table 1). This difference contrasts with other studies which reported similar magnitude of the fluxes measured by chamber and micrometeorological methods$^{14,15}$. Rochette and Eriksen-Hamel$^{16}$ evaluated a data set of 356 studies of chamber measurement of soil N$_2$O, and concluded that the flux data might be valid for comparisons between treatments but could be biased estimates of actual fluxes. These findings indicate that the actual N$_2$O flux estimates obtained by different techniques are not always in good agreement. The following four explanations for the discrepancy in the actual fluxes we measured between the micrometeorological and chamber techniques are feasible. First, the issue of high spatial variability of N$_2$O emission$^{17,18}$ was more likely overcome by paddock-scale measurement using a micrometeorological technique which covered all

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**Figure 1** Effect of DMPP application on N$_2$O emission measured by (a) open-path FTIR spectroscopy (simulated at background N$_2$O concentration enhancement of 5 nmol mol$^{-1}$ with the bLS model) and (b) closed chamber method from the bed and the furrow. Values are the means of five replicates for each treatment. Vertical bars indicate standard errors.

**Table 1** The effect of DMPP application on average N$_2$O flux measured by open-path FTIR spectroscopy (with 0, 5 and 10 nmol mol$^{-1}$ background enhancement) and closed chamber techniques across 8–24 May.

| N$_2$O flux (g N ha$^{-1}$ d$^{-1}$) | Open-path FTIR (with background enhancement, nmol mol$^{-1}$) | Chamber$^a$ (mean ± SE, n = 5) |
|-----------------------------------|-------------------------------------------------|----------------------|
|                                   | 0      | 5      | 10     |                     |
| Control                           | 1053.0 | 317.8  | 168.2  | 23.7 ± 6.8          |
| DMPP                             | 589.5  | 197.3  | 106.9  | 14.7 ± 2.3          |
| % change due to DMPP application | −44    | −38    | −37    | −38 (p = 0.2)       |

$^a$calculated based on the ratio of the width of the bed to that of the furrow (3:1).
N₂O emission ‘hot spots’. Second, the temporal or diurnal variability of N₂O flux was captured by continuous measurements using open-path FTIR spectroscopy while the 1-hour ‘snapshot’ measurements by closed chambers might have excluded any sporadic emission peaks. Third, significant events of N₂O emission associated with water input might have missed out from chamber measurements particularly for vegetable production systems with substantial irrigation. Fourth, the micrometeorological data filtering process for the bLS model excluded data associated with low wind speed (friction velocity ≤ 0.15 m s⁻¹) which was more common at night when the flux was low, thereby possibly overestimating the daily N₂O fluxes. The lack of simultaneous measurements of background N₂O concentration in our study resulted in variation in the absolute N₂O fluxes simulated by the bLS model, but this variation did not invalidate the treatment effects, which was the focus of our study.

In summary, our results indicate that N₂O emission from an intensive vegetable farm can be mitigated by using a nitrification inhibitor. The N₂O fluxes measured by different techniques should be interpreted carefully when making assessments on an absolute scale in national inventories of soil N₂O and in model estimates from agricultural systems. Further study is required to substantiate the contrasting difference in gas measurements by these techniques under a range of agricultural systems and climatic conditions.

Methods

Celery crops 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. The gas measurement was conducted between 6 and 24 May. This was the most intensive period of N application, which encompassed surface application to the celery growing beds of chicken manure (3.4% N) at 255 kg N ha⁻¹ on 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. Two paddocks (243 m × 192 m) in the farm were used for this study, one for the control and the other for DMPP treatment (applied at 6.64 kg ha⁻¹ on 8 May). The soil is classified as a Tenosol with 91% sand. The soil (0–15 cm) has a pH (1:5 soil: water) of 7.9 and contains 0.64% organic carbon. The NH₄⁺ or NO₃⁻ content did not differ between the two paddocks five days after the celery transplant, and ranged from 15.7–16.1 mg N kg⁻¹ and 11.4–11.7 mg N kg⁻¹, respectively.

Details of the technique of open-path FTIR spectroscopy in conjunction with the WindTrax model have been described in ref. 11. Briefly, an open-path 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 910 m. N₂O concentration in the paddock was continuously measured at 30-min intervals. Measured spectra were analyzed at spectral region of 2300 cm⁻¹ using a Multi-Atmospheric Layer Transmission model22 and the high-resolution transmission molecular absorption database23. 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 components covariance and variations, wind speed, wind direction and air temperature, were recorded at 10 Hz. The fluxes of N₂O were simulated at 10-min intervals using the bLS model (WindTrax 2.0, Thunder Bay Scientific) based on any enhancement in N₂O concentration measured in the paddock compared to that outside the paddock (background concentration). While no simultaneous measurements of background N₂O concentration were conducted throughout the study period, the flux calculations would have been affected by any diurnal variation in background concentration. Therefore, based on an average diurnal variation in background N₂O concentration (10 nmol mol⁻¹ observed across one week prior to manure application), we estimated the N₂O fluxes using three background concentrations (0, 5 and 10 nmol mol⁻¹ enhancement).

The fluxes of N₂O were also measured using closed chambers24 (25 cm diameter, 15 cm height) at the control and DMPP-treated paddocks, both in the bed and furrow areas, with five replicates randomly located at where the open-path FTIR measurements were taken. The chambers were inserted to a soil depth of 5 cm. On each sampling day, gas samples (20 mL) were collected between 1300–1600 h at 0, 30 and 60 minutes after chamber closure using a gas-tight syringe, transferred into evacuated 12 mL vials (Extauter™, Labco Ltd.) and analysed by gas chromatography (Agilent 7890A). The flux rates of N₂O were calculated as described in ref. 25. Soil (0–15 cm) samples were collected across each paddock from the bed and furrow areas using a 2.5 cm internal diameter corer. Four replicate samples (a composite of 15 soil cores) were collected by traversing each quadrant of the paddock from the corner to the centre. Subsamples (20 g, dried at 40 °C, <2 mm) were extracted with 100 mL 2 M potassium chloride26. The concentrations of NH₄⁺ and NO₃⁻ in the filtered extract were determined colorimetrically by a segmented flow analyser (Skalar SAN2™). Data of gas fluxes obtained from closed chambers and mineral N were analysed with MINITAB 16 statistical package using a General Linear Model analysis of variance.

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**Acknowledgments**

This work was supported by the Federal Department of Agriculture and the Incitec Pivot Ltd. The authors thank the Lamattina group and Mr Russell Lamattina for the use of their farm, Dr Arvin Mosier for his constructive comments on the manuscript, Dr Thomas Flesch for his valuable advice on micrometeorological data processing, Dr Robert Edis, Mr David Riches, Mr Ben Grasso, Mr Trevor Coates, Mr Muhammad Shakir, Mr Paul Jaques, Dr Jagrati Singh and Dr Xing Chen for field assistance, soil chemical and gas analyses.

**Author contributions**

D.C., H.S., R.D. and S.K.L. designed the investigation. S.K.L., H.S., M.B. and J.S. conducted the field experiment. S.K.L., H.S., D.C. and M.B. interpreted the data. All authors were involved in writing the paper.

**Additional information**

Competing financial interests: The authors declare no competing financial interests.

*How to cite this article:* Lam, S.K. et al. Measurement and mitigation of nitrous oxide emissions from a high nitrogen input vegetable system. *Sci. Rep.* **5**, 8208; DOI:10.1038/srep08208 (2015).

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Author/s:
Lam, SK; Suter, H; Davies, R; Bai, M; Sun, J; Chen, D

Title:
Measurement and mitigation of nitrous oxide emissions from a high nitrogen input vegetable system

Date:
2015-02-03

Citation:
Lam, S. K., 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 (1), https://doi.org/10.1038/srep08208.

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