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Title:

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Date:

2017-02-01

Citation:

Lam, S. K., Suter, H., Mosier, A. R. & Chen, D. (2017). Using nitrification inhibitors to mitigate agricultural N₂O emission: a double-edged sword?. *Global Change Biology*, 23 (2), pp.485-489. <https://doi.org/10.1111/gcb.13338>.

Persistent Link:

<https://hdl.handle.net/11343/291946>

Received Date : 25-Feb-2016

Accepted Date : 28-Apr-2016

Article type : Opinion

Title page

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Using nitrification inhibitors to mitigate agricultural N₂O emission: a double-edged sword?

Running head

Dual effect of nitrification inhibitor on N₂O

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Keywords

Nitrification inhibitor, nitrous oxide, ammonia, indirect greenhouse gas, agriculture, climate change mitigation

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the [Version of Record](#). Please cite this article as [doi: 10.1111/gcb.13338](https://doi.org/10.1111/gcb.13338)

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Type of Paper

Opinion

Abstract

Nitrification inhibitors show promise in decreasing nitrous oxide (N_2O) emission from agricultural systems worldwide, but they may be much less effective than previously thought when both direct and indirect emissions are taken into account. Whilst nitrification inhibitors are effective at decreasing direct N_2O emission and nitrate (NO_3^-) leaching, limited studies suggest that they may increase ammonia (NH_3) volatilization and subsequently, indirect N_2O emission. These dual effects are typically not considered when evaluating the inhibitors as a climate change mitigation tool. Here we collate results from the literature that simultaneously examined the effects of nitrification inhibitors on N_2O and NH_3 emissions. We found that nitrification inhibitors decreased direct N_2O emission by 0.2–4.5 kg N_2O -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_2O emission from deposited NH_3 , the overall impact of nitrification inhibitors ranged from –4.5 (reduction) to +0.5 (increase) kg N_2O -N ha^{-1} . Our results suggest that the beneficial effect of nitrification inhibitors in decreasing direct N_2O emission can be undermined or even outweighed by an increase in NH_3 volatilization.

Introduction

Globally, agriculture contributes about 60% of the total anthropogenic emission of nitrous oxide (N_2O), a greenhouse gas approximately 300 times more potent than carbon dioxide (Ciais *et al.*, 2013). The mitigation of N_2O emission from agricultural systems is an important issue worldwide. Nitrification inhibitors are recommended by the IPCC as a potential mitigation option for agricultural N_2O emission (IPCC, 2014), and have been extensively investigated and widely used across a broad range of agroecosystems (Chen *et al.*, 2008; Qiao *et al.*, 2015). Nitrification inhibitors temporarily suppress the microbial conversion of ammonium (NH_4^+) to nitrite (NO_2^-) in soil. This reduces substrate availability for nitrate (NO_3^-) formation and subsequent denitrification, thereby decreasing N_2O emission and NO_3^- leaching (Bundy & Bremner, 1973; Chen *et al.*, 2008). Recent meta-analyses indicated that nitrification inhibitors decreased N_2O emission and NO_3^- leaching by 31–48% and 32–59%, respectively, across diverse agricultural ecosystems including upland, grassland and paddy fields (Akiyama *et al.*, 2010; Qiao *et al.*, 2015). Nitrate lost via leaching and runoff may be transported to groundwater, rivers or estuaries where part of it may be

converted to N₂O (Nevison, 2000). This indirect N₂O emission can be estimated by the IPCC emission factor EF₅ with a default value of 0.75% (De Klein *et al.*, 2006).

The use of nitrification inhibitors, however, prolongs the retention of NH₄⁺ in soil, which could potentially increase ammonia (NH₃) emission (Zaman & Nguyen, 2012). Deposition of emitted NH₃ not only poses a major threat to environmental quality and ecosystem biodiversity (Erisman *et al.*, 2008), but indirectly it also contributes to N₂O emission (van der Gon & Bleeker, 2005) through subsequent nitrification and denitrification. According to the IPCC guidelines (De Klein *et al.*, 2006), about 1% (a range of 0.2–5%) of the NH₃ emitted is converted to N₂O after deposition to land (IPCC emission factor EF₄).

While the effect of nitrification inhibitors on NH₃ volatilization is not as widely studied as that on N₂O emission, Qiao *et al.* (2015) recently summarized the available studies and concluded that nitrification inhibitors increased NH₃ volatilization from synthetic fertilizers and animal manures in agricultural systems by 33–67%. However most of the studies included in the synthesis focussed on one or other of these gases, and Qiao *et al.* (2015) expressed the impact of the inhibitor as percentage change, not absolute difference, in nitrogen (N). The overall inhibitor effect on N₂O emission (direct and indirect), which can be determined from studies that simultaneously measure N₂O and NH₃ emissions and NO₃⁻ leaching in the field, remains uncertain. The inclusion of indirect N₂O emission is critical for evaluating the effectiveness of nitrification inhibitors in mitigating greenhouse gas emissions from agriculture. We therefore conducted a literature review to address this knowledge gap.

Literature search

To assess the overall contribution of nitrification inhibitors to N₂O emission (direct and indirect), we performed extensive keyword searches of several databases (Web of Science, Scopus, CAB Abstracts, Academic Search complete and Google Scholar), and the reference list of cited references, for studies published prior to October 2015. The keywords used in the search included nitrification inhibitors, names of the inhibitors such as DCD and DMPP, nitrous oxide/N₂O emission, ammonia/NH₃ emission, volatilization, direct/indirect N₂O, greenhouse gas, nitrate/NO₃⁻ leaching, loss and/or mitigation, agriculture, cropping, pastures, and their combinations. Only studies that simultaneously examined N₂O and NH₃ emissions in the same field location were included. The search resulted in 18 observations in pasture and cropping systems (Table 1).

99 **Dual effects of nitrification inhibitors on N₂O emission**

100 From the literature review, we found that nitrification inhibitors consistently decreased direct
 101 N₂O emission from fertilizers (urea and ammonium based) and animal wastes (slurry and
 102 urine), applied at between 97 and 625 kg N ha⁻¹, by 0.2–4.5 kg N₂O-N ha⁻¹ (8–57%) (Table
 103 1). On the other hand, NH₃ volatilization was increased by 0.2–18.7 kg NH₃-N ha⁻¹ (3–65%)
 104 following the application of the inhibitors in all but three observations. Applying the default
 105 emission factor value of 1% (De Klein *et al.*, 2006) for indirect N₂O emission from NH₃
 106 volatilization and deposition (EF₄), we found there was an overall N₂O-N reduction of 0.1–
 107 4.5 kg N ha⁻¹ from the use of nitrification inhibitors. However, when the upper range of EF₄
 108 (5%) (De Klein *et al.*, 2006) was used, the change in N₂O-N ranged from –4.4 (reduction) to
 109 +0.5 (increase) kg N ha⁻¹ (Table 1).

110

111 We found that only two studies reported the effect of nitrification inhibitors on NO₃⁻ leaching
 112 in addition to that on N₂O and NH₃ emissions. This precludes the estimation of indirect N₂O
 113 emission from measured NO₃⁻ leaching for the studies included in Table 1. Nonetheless,
 114 NO₃⁻ leaching is assumed to be an insignificant source of indirect N₂O emission in dryland
 115 cropping systems, and grassland systems where the amount of precipitation plus irrigation
 116 does not exceed 80% of the potential evapotranspiration (IPCC, 2006; U.S. EPA, 2014). A
 117 global process-based simulation of terrestrial N cycle estimated that the annual leaching load
 118 is around 20 kg N ha⁻¹ for most regions with fertilizer application of >100 kg N ha⁻¹. Based
 119 on the default EF₅ value of 0.75% (De Klein *et al.*, 2006), and an average reduction in NO₃⁻
 120 leaching of 47% by nitrification inhibitors (Qiao *et al.*, 2015), we estimated that the inhibitors
 121 may decrease indirect N₂O emission associated with NO₃⁻ leaching by 0.07 kg N ha⁻¹ or
 122 have no effect on the emission when NO₃⁻ leaching is negligible. This has minimal impact on
 123 the overall effect of nitrification inhibitors on N₂O emission.

124

125 The results of our literature review (Table 1) indicate that nitrification inhibitors effectively
 126 and consistently decrease direct N₂O emission from agricultural systems. Nonetheless, this
 127 beneficial effect can be weakened, negated or even reversed by the estimated concomitant
 128 increase in indirect N₂O emission from deposited NH₃. This highlights the importance of
 129 considering both gases when evaluating the use of nitrification inhibitors as a climate change
 130 mitigation option. An alternative approach would be to use a double inhibitor (a combination
 131 of a nitrification inhibitor and urease inhibitor). Urease inhibitors slow the hydrolysis of urea

and consequently reduce NH_3 volatilization and can be effective on urea (Chen *et al.*, 2008). A recent study showed that both NH_3 volatilization and N_2O emission were decreased when urea was treated with a double inhibitor (Zaman & Blennerhassett, 2010). However this double inhibitor approach is impractical for decreasing NH_3 volatilization from N sources containing negligible urea but high NH_4^+ content, such as animal manure and ammonium fertilizers. In this regard, substances with a high affinity for binding onto NH_4^+ ions may be used as additives to mitigate NH_3 volatilization. For instance, zeolite and, more recently, lignite were shown to effectively lower NH_3 volatilization when mixed with animal manure (Ndegwa *et al.*, 2008; Chen *et al.*, 2015). Alternatively, where practical, manure should be incorporated into soil rather than being surface applied to prevent NH_3 loss.

Summary and implication

Nitrification inhibitors decrease direct N_2O emission and indirect N_2O emission due to NO_3^- leaching from agroecosystems. Yet this beneficial effect is weakened by any accompanying increase in indirect N_2O emission that can result from increased emission and deposition of NH_3 . Appropriate NH_3 mitigation measures should be taken where nitrification inhibitors are being used to decrease direct N_2O emissions, to enable effective and viable climate change mitigation.

Acknowledgements

This work was supported by the BIP reinvestment funds of the Faculty of Veterinary and Agricultural Sciences of the University of Melbourne, and the Australia-China Joint Research Centre jointly funded by Australian Government Department of Industry and Science, and the Chinese Ministry of Science and Technology.

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Tables

Table 1 Summary of studies that simultaneously investigated the effects of nitrification inhibitors on N₂O and NH₃ emissions, and the estimated overall impacts

Agricultural system	N form	N rate kg N ha ⁻¹	Season	Inhibitor	Effect of nitrification inhibitor (NI)				Overall NI effect on N ₂ O emission		Country	Gas measurement technique		Reference
					Direct N ₂ O emission		NH ₃ volatilization					N ₂ O	NH ₃	
					% ^a	Amount ^b (kg N ha ⁻¹) (I)	% ^c	Amount ^d (kg N ha ⁻¹) (II)	(kg N ha ⁻¹) (I + II × EF ₄) ^e					
									EF ₄ = 1%	EF ₄ = 5%				
Cropping-rice	urea	180	summer	N-serve	-49.9	-0.57	+64.9	+12.75	-0.44	+0.07	China	CC	OC	Sun <i>et al.</i> , 2015
Cropping-rice	urea	240	summer	N-serve	-19.2	-0.27	+37.5	+15.80	-0.11	+0.52	China	CC	OC	Sun <i>et al.</i> , 2015
Cropping-maize	slurry	165	summer	DCD	-20.4	-0.79	-3.7	-0.40	-0.79	-0.81	Brazil	CC	CC	Aita <i>et al.</i> , 2015
Cropping-wheat	slurry	135	winter	DCD	-52.3	-1.36	+3.1	+0.35	-1.35	-1.34	Brazil	CC	CC	Aita <i>et al.</i> , 2015
Cropping-wheat/barley; pasture	urea	120–200	whole year	DCD	-46.5	-0.52	+6.1	+2.20	-0.50	-0.41	UK	CC	WT	Misselbrook <i>et al.</i> , 2014
Cropping-wheat/barley; pasture	AN	120–200	whole year	DCD	-28.7	-0.48	+5.4	+0.15	-0.48	-0.47	UK	CC	WT	Misselbrook <i>et al.</i> , 2014
Pasture	urine	365–625	spring-autumn	DCD	-56.8	-1.24	-0.8	-0.97	-1.25	-1.29	UK	CC	WT	Misselbrook <i>et al.</i> , 2014
Pasture	urine	365–625	spring-autumn	PD	-10.6	-0.23	+4.0	+4.87	-0.18	+0.01	UK	CC	WT	Misselbrook <i>et al.</i> , 2014
Pasture	slurry	106–181	spring/autumn	DCD	-30.1	-0.38	+7.7	+2.55	-0.36	-0.26	UK	CC	WT	Misselbrook <i>et al.</i> , 2014
Pasture	urine	600	autumn	DCD	-42.1	-2.93	+35.5	+18.65	-2.74	-2.00	New Zealand	CC	OC	Zaman <i>et al.</i> , 2013
Pasture	urine	600	spring	DCD	-40.5	-2.15	+13.3	+13.87	-2.01	-1.46	New Zealand	CC	OC	Zaman <i>et al.</i> , 2013
Pasture	urine	600	autumn	DCD	-37.1	-4.47	+43.4	+12.60	-4.34	-3.84	New Zealand	CC	OC	Zaman & Blennerhassett 2010
Pasture	urine	600	spring	DCD	-46.8	-4.33	+18.2	+8.00	-4.25	-3.93	New Zealand	CC	OC	Zaman & Blennerhassett 2010
Pasture	urine	600	spring	DCD	-38.6	-4.40	+9.1	+2.00	-4.38	-4.30	New Zealand	CC	OC	Zaman <i>et al.</i> , 2009
Pasture	urine	600	summer	DCD	-20.0	-0.30	+17.2	+8.60	-0.21	+0.13	New Zealand	CC	OC	Zaman <i>et al.</i> , 2009
Pasture	slurry	123	spring-summer	DMPP	-7.9	-0.18	+13.9	+1.80	-0.16	-0.09	Spain	CC	OC	Menéndez <i>et al.</i> , 2009
Pasture	ANS	97	spring	DMPP	-8.8	-0.39	-51.7	-0.15	-0.39	-0.40	Spain	CC	OC	Menéndez <i>et al.</i> , 2006
Pasture	slurry	181	spring	DMPP	-29.1	-4.51	+42.0	+3.16	-4.48	-4.35	Spain	CC	OC	Menéndez <i>et al.</i> , 2006

^a The value was calculated by: (N₂O emission in the treatment with NI – N₂O emission in the control) / N₂O emission in the control × 100%

^b The value was calculated by: N₂O emission in the treatment with NI – N₂O emission in the control

^c The value was calculated by: (NH₃ volatilization in the treatment with NI – NH₃ volatilization in the control) / NH₃ volatilization in the control × 100%

^d The value was calculated by: NH₃ volatilization in the treatment with NI – NH₃ volatilization in the control

^e EF₄ of 1% and 5% represent the mean and upper range, respectively, of the IPCC default emission factor for indirect N₂O emission¹⁴

AN: ammonium nitrate

ANS ammonium nitrate sulphate

CC: closed chamber

DCD: dicyandiamide

DMPP: 3,4-dimethylpyrazole phosphate

EF₄: emission factor for indirect N₂O emission

NI: nitrification inhibitor

OC: open chamber

PD: pyrazole derivatives 1H-1,2,4-triazole and 3-methylpyrazole

WT: wind tunnel