Science of the Total Environment 465 (2013) 136–146

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Quantification of reductions in ammonia emissions from fertiliser urea and animal urine in grazed pastures with urease inhibitors for agriculture inventory: New Zealand as a case study

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HIGHLIGHTS

- We comprehensively review the efficacy of urease inhibitors in reducing ammonia losses from soils.
- We assess the merits of applying urease inhibitors to grazed-pastures either with urea fertilisers or by themselves.
- We provide a method to quantify ammonia emission from fertiliser N for the national agriculture greenhouse gas inventory.

ARTICLE INFO

Article history:
Received 9 May 2012
Received in revised form 23 July 2012
Accepted 27 July 2012
Available online 7 September 2012

Keywords:
Ammonia emissions
$Frac_{GASF}$
$Frac_{GASM}$
Nitrous oxide emission
N-(nbutyl) thiophosphoric triamide (nBTPT)
Urease inhibitors

ABSTRACT

Urea is the key nitrogen (N) fertiliser for grazed pastures, and is also present in excreted animal urine. In soil, urea hydrolyses rapidly to ammonium (NH_4^+) and may be lost as ammonia (NH_3) gas. Unlike nitrous oxide (N_2O), however, NH_3 is not a greenhouse gas although it can act as a secondary source of N_2O, and hence contribute indirectly to global warming and stratospheric ozone depletion. Various urease inhibitors (UIs) have been used over the last 30 years to reduce NH_3 losses. Among these, N-(n-butyl) thiophosphoric triamide (nBTPT), sold under the trade name Agrotain®, is currently the most promising and effective when applied with urea or urine. Here we conduct a critical analysis of the published and non-published data on the effectiveness of nBTPT in reducing NH_3 emission, from which adjusted values for $Frac_{GASF}$ (fraction of total N fertiliser emitted as NH_3) and $Frac_{GASM}$ (fraction of total N from, animal manure and urine emitted as NH_3) for the national agriculture greenhouse gas (GHG) inventory are recommended in order to provide accurate data for the inventory. We use New Zealand as a case study to assess and quantify the overall reduction in NH_3 emission from urea and animal urine with the application of UI nBTPT.

The available literature indicates that an application rate of 0.025% w/w (nBTPT per unit of N) is optimum for reducing NH_3 emissions from temperate grasslands. UI-treated urine studies gave highly variable reductions (11–93%) with an average of 53% and a 95% confidence interval of 33–73%. New Zealand studies, using UI-treated urea, suggest that nBTPT (0.025% w/w) reduces NH_3 emissions by 44.7%, on average, with a confidence interval of 39–50%. On this basis, a New Zealand specific value of 0.055 for $Frac_{GASF}$ FN_{UI} (fraction of urease inhibitor treated total fertiliser N emitted as NH_3) is recommended for adoption where urea containing UI are applied as nBTPT at a rate of 0.025% w/w. Only a limited number of published data sets are available on the effectiveness of UI for reducing NH_3 losses from animal urine-N deposited during grazing in a grazed pasture system. The same can be said about mixing UI with urine, rather than spraying UI before or after urine application. Since it was not possible to accurately measure the efficacy of UI in reducing NH_3 emissions from animal urine-N deposited during grazing, we currently cannot recommend the adoption of a $Frac_{GASM}$ value adjusted for the inclusion of UI.

1. Introduction

Urea is the most common source of fertiliser nitrogen (N), meeting almost half of the world's N requirement. Continued growth is

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http://dx.doi.org/10.1016/j.scitotenv.2012.07.088

expected in the use of urea fertiliser owing to its high-N content and ease of application in a dry granular form or as an aqueous solution. The increased use of urea-based fertilisers (solid or liquid), however, would increase NH_3 emissions to the atmosphere. In intensively managed grazed pastures, animal urine also contributes substantially to NH_3 emissions with a single urination event depositing 300–1000 kg N/ha (Haynes and Williams, 1993; Jarvis et al., 1995), which is well above the N requirement of pastures (Blennerhassett et al., 2006). The excess of readily available N in urine patches and the increased application of N fertiliser (predominantly urea; 80%) to pastures in New Zealand cause atmospheric pollution through nitrous oxide (N_2O) and ammonia (NH_3) emissions, and aquatic pollution through nitrate (NO_3) leaching (Saggar et al., 2005).

Unlike N_2O, NH_3 itself is not a greenhouse gas (GHG) but can act as a secondary source of N_2O (Martikainen, 1985) by conversion to NO_3 and dinitrogen (N_2) through nitrification and denitrification following downwind deposition. Ammonia may therefore contribute indirectly to global warming and ozone (O_3) depletion in the atmosphere. Ammonia emissions also represent agronomic losses and may cause eutrophication of aquatic systems and soil acidification after deposition on water and soil (Bobbink et al., 1992; Barthelmie and Pryor, 1998; van der Eerden et al., 1998; Zaman et al., 2008, 2009; Zaman and Blennerhassett, 2010; Sanz-Cobena et al., 2012).

Based on the review of emission factors by Sherlock et al. (2008), the New Zealand Ministry of Agriculture & Forestry (MAF; now Ministry for Primary Industries; MPI) has recommended a specific value of 0.1 for both $Frac_{GASF}$ (fraction of total N fertiliser emitted as nitrogen oxides (NO_x) and NH_3) and $Frac_{GASM}$ (fraction of total N from, animal manure and urine emitted as NO_x and NH_3). This specific value has been adopted in the national GHG inventory calculation as reported annually to the United Nations Framework Convention on Climate Change (UNFCCC) (MfE, Ministry for the Environment, 2012). Using a 10% emission factor (EF) for NH_3 (Sherlock et al., 2008), it is estimated that New Zealand grazed pastures lose 0.13 Gg of N as NH_3 on an annual basis from deposition of urine, and applied fertilisers and farm dairy effluent.

Various approaches to mitigating NH_3 losses have been investigated within New Zealand, one of which is the use of urease inhibitors (UIs). In New Zealand the use of commercially formulated fertilisers containing UIs, notably urea treated with Agrotain® (trade name — SustaiN) and urea coated with Agrotain®, elemental S and lime (trade name — PhasedN) is increasing; the sale of Agrotain®-treated urea increased by 81% from 12 Gg N in 2008 to 22 Gg N in 2010.

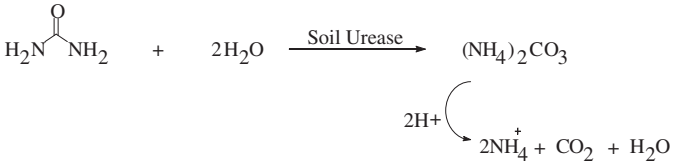
A number of studies have found that the application of UIs with N-fertilisers and animal urine can further reduce NH_3 emission (Singh, 2007; Zaman et al., 2008, 2009; Zaman and Blennerhassett, 2010), and hence the current values of $Frac_{GASF}$ and $Frac_{GASM}$ (Saggar et al., 2009, 2011). No country has yet revised its emission factors to account for the effect of UI-treated urea or UI-treated soils.

For inventory purposes, it is necessary that emission reductions from the use of UIs are quantified and that specific $Frac_{GASF}$ and $Frac_{GASM}$ values are developed.

This paper i) reviews the published and unpublished information from New Zealand and overseas on the efficacy of UIs in reducing NH_3 losses; ii) assesses the merits of applying UIs to soils either combined with urea fertilisers or by themselves; iii) examines the factors (quantities of inhibitors, soil types, regions, grazing regimes) affecting the role of UIs in N transformation; and iv) suggests a methodological approach to quantifying ammonia emissions for the national agriculture greenhouse gas inventory. Although we aim to review processes, compounds and factors that are globally relevant to regulating urease inhibition and NH_3 emission, we use New Zealand as a case study.

2. Ammonia emission processes

Urea applied to soils in the form of fertiliser or deposited in animal urine is usually rapidly hydrolysed within 1–2 days (Zaman et al., 2008) to ammonium carbonate which, in turn, decomposes to carbon dioxide (CO_2) and ammonium (NH_4^+) (Bolan et al., 2004). The hydrolysis reaction, catalysed by the enzyme urease (Eq. (1)), is temperature dependent.



(Eq. 1)

The rate of hydrolysis increases with soil temperature over the range of 0–40 °C (Vlek and Carter, 1983). Nevertheless, considerable urea hydrolysis has been detected at sub-zero temperatures (Bremner and Mulvaney, 1978; Engel et al., 2011). The hydrolysis of urea is promoted by a high biological activity at the soil surface (Zaman et al., 2002), leading to large losses of NH_3 (30–44% of applied N) (Engel et al., 2011; Sanz-Cobena et al., 2012). Urea hydrolysis below the soil surface favours conversion of NH_3 to NH_4^+ which then binds to soil particles. In highly porous soils urea can move down the profile and be lost by burial (Rochette et al., 2009).

Under alkaline conditions, NH_4^+ is converted to ammonia which is then volatilised. The potential loss of urea-N by volatilisation is regulated by many factors, including soil temperature, water content, cation exchange capacity (CEC), wind speed, pH and the presence of free NH_3 near the soil surface (Bolan et al., 2004). The amount of plant canopy and surface plant residue together with the length of time between urea application and the first rain event or irrigation also influence the total amount of NH_3 that can potentially be emitted (Black et al., 1987).

Studies conducted in New Zealand and worldwide have shown that urea-containing fertilisers can lose 30% or more of their N as NH_3 unless they are rapidly incorporated into the soils. Black et al. (1985) found that the proportion of NH_3 lost increases with the rate of urea-N application. In New Zealand, NH_3 emissions range from c. 11% at rates of ≤45 kg N/ha of urea-N, typically used for grazed pastures to c. 30% at a rate of 300 kg N/ha (Sherlock et al., 2008). Ammonia losses are expected to be low from urine deposition as compared with those from surface applied urea as most of the urine from grazing animals is rapidly incorporated into the soil. Studies in New Zealand by Sherlock et al. (2008), using aspirated chambers, suggest that the direct NH_3-N emissions from urine applied to pasture soils average 15.9%. Using the mass budget method, Laubach et al. (2012) found that 25.7 (±0.5) % of applied urine was emitted as NH_3 during the first 6 days following application at mean soil temperature of 18 °C. These measurements were made during the warmest time of the year and these emission rates represent the upper end of the range that can occur in New Zealand. After accounting for the correlation between temperature and emission rate, the observed emission rates were compatible with an annually-averaged emission factor, $Frac_{GASM}$, of 10% for urine and dung combined.

2.1. Urease activity

The urease enzymes are synthesised by plants, fungi and bacteria but not by animals. Ureases are widespread in nature. Plant and fungal ureases are trimers or hexamers of a single type of ~90 kDa subunit with about 840 amino acids. In contrast bacterial ureases are multimers