Physical and chemical manipulation of urea fertiliser for reducing the emission of gaseous nitrogen species

M. I. Khalil[A]

[A]School of Biology and Environmental Science, University College Dublin, Belfield, Dublin 4, Ireland.
Climate Change Research, Environmental Protection Agency, Johnstown Castle Estate, Wexford, Ireland (E-mail: i.khalil@epa.ie).

Abstract

Concerning environmental consequences, technological attempts to decrease reactive N species emitted by the application of urea fertiliser to agricultural soils are being continued. To find suitable mitigation options, urea size and placement depths as well as new inhibitors of various chemical origins were tested in loess soil cropped to spring wheat under greenhouse conditions. Relatively a larger urea granule (USG; ≤0.7 g) inhibited nitrification up to 7 weeks and reduced both NH_3 and NO_x emissions up to 94%. Under cropped conditions, the USG point-placed at 7.5 cm depth showed similar response to urea prills on N_2O emissions (0.20-0.21% of the added N) though increased to 0.53% at relatively higher soil moisture content. Urease inhibitor (substituted phosphoric acid triamide) decreased NH_3 losses substantially (60%), and also N_2O (47%) when mixed into soil. Nitrification inhibitor (Dicyanamide plus triazole)-amended urea inhibited nitrification up to 5 weeks and reduced N_2O emission from 20 to 60%. A combination of urease and nitrification inhibitors-included urea decreased both NH_3 (60%) and N_2O (25-52%) losses. Results imply that both approaches could mitigate substantially the urea-induced emissions of reactive N species.

Key Words

Nitrogen fertiliser, trace gases, mitigations, cambisol, arable crop.

Introduction

Reactive N species viz. N_2O, NH_3 and NO_x have large potentials for global warming, stratospheric ozone layer depletion and acid deposition. Technological attempts are being continued to reduce their emission from agricultural soils where urea, as the cheapest and mostly used N fertiliser globally (>50%; IFA, 2010), seems to take a major share. As an alkaline-hydrolyzing N fertilizer, urea (prills/small granules) influences nitrification through a transient rise in pH with subsequent denitrification leading to the formation and release of large volumes of N_2O (Mulvaney *et al.* 1997; Khalil *et al.* 2002) as well as NH_3 and NO_x when broadcast (Khalil *et al.* 2006; 2009a). In the placement zone of USG, high localized urea/NH_4^+ and NO_2^- levels and soil pHs develop through enzyme-catalysed urea hydrolysis and diffuse slowly outward under aerobic conditions. This results in either little or no immobilization initially and inhibits both urease and nitrifier activity (Shah and Wolfe 2003) and thus reduces gaseous N emissions (Khalil *et al.* 2006; 2009 a,b).

Numerous urease and nitrification inhibitors or their combination of different chemical origins found to be effective in reducing NH_3 volatilization and N_2O emissions from agricultural soils. Nitrification inhibitor dicyandiamide (DCD)-amended urea can reduce N_2O emission largely but its affectivity in limiting NH_4^+ oxidation was short-term compared to 3,4-dimethypyrazole phosphate (DMPP) (Linzmeier *et al.* 2001; Majumdar *et al.* 2002). The lower efficacy and higher volatility, instability and decomposition rate of a sole compound lead to apply larger dosage but the combination of two would enhance nitrification inhibition efficiency and allow to reduce the dosage. Besides, a combination of urease and nitrification inhibitors amended with urea can be useful to reduce both NH_3 and N_2O losses (Boeckx *et al.* 2005; Schraml *et al.* 2005). A combination of urease (P204/98) and nitrification (DCD/TZ) inhibitor, which is larger (2-3 mm) than urea prills, could reduce NH_3 loss (Schraml *et al.* 2005) and N_2O emission by inhibiting nitrification (Khalil *et al.* 2009c). This paper deals with a comparison between the above-mentioned physical and chemical manipulation of urea fertilizer in reducing the reactive N species.

Materials and methods

The soil used for experiments done in Germany was a loess silt loam (20% sand, 60% silt and 20% clay; Cambisol). It had a pH_{H2O} of 6.4, a CEC of 17.6 $cmol_c$ (+)/kg soil and a C/N ratio of 9.5 (0.17% N and 1.61% organic C). Under aerobic conditions, several laboratory and greenhouse investigations were carried out with urea granule sizes, placement depths, soil types (sandy loam, silt loam and clay loam), and urease and nitrification inhibitors and their combination with or without spring wheat (Khalil *et al.* 2006; 2009 a,c).

Under greenhouse conditions, polyvinyl boxes (110 cm x 70 cm x 40 cm) were filled with 5 cm of sand on the bottom, followed by 20 cm and 15 cm of subsurface and surface soils, respectively. Here, the following experiments are illustrated but comparisons with others done are also made in the results and discussion.

Urea super granules on N_2O, NH_3 and NO_x emissions

The treatments of this experiment to measure N_2O emissions were N_0 - unfertilised control, PU - prilled urea (<1 mm) mixed homogenously with the soil, and $USG_{7.5}$- urea super granule (dia. 10.1 mm; wt. ~0.69 g/USG) point-placed at 7.5 cm depth. The PU labeled with ^{15}N (2.9 atom %) and USG, which was prepared from the former using a mechanical press, were applied at 88.15 kg N/ha. The cumulative amount of water added was 320 L over 116 days of wheat growth period. Another experiment was conducted to measure N_2O, NH_3 and NO_x emissions during a 70-day growth period with treatments: unfertilised control (N_0), USG point-placed at 2.5 ($USG_{2.5}$), 5 ($USG_{5.0}$) and 7.5 cm ($USG_{7.5}$) soil depths. Urea-N labeled with ^{15}N (5.1 atom%) was applied at 91.74 kg N/ha. Water depletion was slower, with the total amount of water added being 120 L in 70 days, presumably due to initial stunted plant growth and lower evaporative demands associated with this experiment being performed in the winter.

Inhibitors-amended urea and granular size for N_2O emissions

The treatments of this experiment were unfertilized control, PU, urea granule (GU), USG, urease inhibitor (UI), and the combination of urease and nitrification inhibitors (UNI). The nitrification inhibitor (NI) treatment was not included as the response was similar to the UNI under laboratory conditions (Khalil *et al.* 2009c). The USGs were point-placed at 5 cm depth, and soil was mixed down to a 5 cm depth for the other treatments and urea was applied at 88.2 kg N/ha. The cumulative amount of water added was 170 L over 70 days. Spring wheat experienced all natural weather conditions except rainfall.

Gas samplings, measurement and statistics

Gas for N_2O was collected using a closed chamber method and measured using an automated gas chromatography (Varian Star 3400, USA) equipped with electron capture and its ^{15}N abundance was measured using GC-IRMS. NH_3 and NO_x were measured simultaneously by flowing the sample air to a two-channel chemiluminescence NO-Analyser (CLD 700AL, Fa. EcoPhysics, Gürnten, CH). Statistical analyses were performed using the computer package JMP v4.0.2 of SAS Inc. Total gaseous emissions were calculated by integrating the area of the daily fluxes. Relative and actual N_2O losses of the added N were calculated based on its total fluxes from the control.

Results and discussion

The USG, in general, delayed N_2O emissions for 2-3 weeks, emitting almost similar amount (relative losses of 0.20-0.21% or 0.01% of the added ^{15}N) with the USG placed at 7.5 cm soil depth to PU under controlled soil water conditions (Khalil *et al.* 2009a). In the experiment with various USG placement depths, higher water content somewhat enhanced N_2O emission (0.50-0.73%), in line with Khalil *et al.* (2009b), following fertilization to wheat (Table 1). Overall, N_2O emissions somewhat increased with increasing USG placement depths (Tenuta and Beauchamp 2000; Khalil *et al.* 2006; 2009b). The contribution of added ^{15}N to N_2O emissions decreased over time and was small (0.02-0.15%), indicating soil N as the major source (Linzmeier *et al.* 2001). However, the emission factors were much lower than the IPCC default (1.25%), signifying the large potential of USG in reducing N_2O emission. This is in agreement with Khalil *et al.* (2006) but with the exact effect being soil-specific as fine-textured soil may exacerbate N_2O emission.

Table 1. Total N_2O over 70 days, and NH_3 and NO_x emissions over 43 days growth period of spring wheat, and their relative losses of added N as influenced by placement depths of urea super granules.

Treatments	N_2O emission		NH_3 volatilisation		NO_x emission	
	Total emission (g N/ha)	Relative loss (%)	Total volatilized (g N/ha)	Relative loss (%)	Total flux (g N/ha)	Relative loss (%)
USG-2.5	737.0	0.67	1071.8	1.22	1409.4	1.60
USG-5.0	787.3	0.73	230.2	0.26	1116.5	1.27
USG-7.5	607.4	0.53	61.9	0.07	178.8	0.20
$LSD_{0.05}$	242.0	ns	-	-	-	-

USG-2.5, 5.0 and 7.5 = urea super granule point-placed at 2.5, 5.0 and 7.5 cm soil depths; LSD = least significant difference at 5% level (after Khalil *et al.* 2009a)

The maximum NH_3 volatilization was detected within 8-15 day after fertilisation (DAF) and declined with increasing USG placement depths, ranged from 0.07 to 1.22%, and the deeper placement decreased it by 79-94% over the shallower placement. This larger NH_3 emission seems to be associated with shallower placement of USG under aerobic conditions. This finding is in agreement with others (Bouwmeester *et al.* 1985; Khalil *et al.* 2006), apparently relating to vapour diffusion from USG-induced high NH_4^+ concentration that was placed next to the soil surface. The mixing of PU deeper into the soil might reduce NH_3 volatilization greatly as for USG point-placed and/or banding of urea at a certain depth into consideration (Sommer *et al.* 2004; Khalil *et al.* 2006, 2009b). Soils having high H^+ buffering capacities might prevail over the high concentration gradients of NH_4^+ and pH, which occurs in the placement zone only (Khalil *et al.* 2006; 2009b), leading to the fixation of NH_3 vapour within the upper soil.

The trends for NO_x emission, peaked after 23 DAF, were similar to NH_3 volatilization (Khalil *et al.* 2009a), as they are interactively favoured by similar soil and environmental conditions (Khalil *et al.* 2006). The deeper USG placements reduced total NO_x emission by 23 and 88% over the shallower placement. Hou and Tsuruta (2003) reported similar results through band placement of urea at a 12-cm depth. The presence of comparatively more NH_4^+ for subsequent nitrification in the surface than the sub-surface layers could possibly influence NO_x emission (Khalil *et al.* 2006). The point-placed USG decreased NH_3 and NO_x losses by placing in deeper soil layers and also the total gaseous N ($N_2O + NH_3 + NO_x$) losses.

Experiments with inhibitors versus USG under cropped conditions showed that the PU emitted smaller N_2O than the GU or USG but varied insignificantly (Table 2). This was probably linked to faster immobilization upon fertilisation and thereby the presence of mineral N at a lower amount. Khalil *et al.* (2006) also reported that N_2O emission increases with increasing urea granule size. The soil mixed UI could reduce N_2O emission by two-fold over the GU, presumably due to the delayed hydrolysis and thus restricted nitrification in the beginning, in agreement with Boeckx *et al.* (2005) who used hydroquinone (HQ). However, the broadcast UI limiting NH_3 volatilization might exacerbate N_2O emission by 47% (Khalil *et al.* 2009c).

Table 2. Total N_2O fluxes and the relative N_2O loss of added N from a loess soil at varying urea size, UI and UNI under greenhouse conditions with spring wheat.

Treatments		Control	PU (<1 mm)	GU (2-3 mm)	USG (~10 mm)	UI (as GU)	UNI (as UI+NI)	$LSD_{0.05}$
Total N_2O flux	45 day	130.3	254.6	338.7	314.2	202.8	146.0	135.7
(g N/ha)	70 day	186.3	325.0	386.7	424.5	294.6	284.1	ns
Relative loss	45 day		0.14	0.24	0.21	0.08	0.02	0.20
of added N (%)	70 day		0.16	0.23	0.27	0.12	0.11	ns

Control = No N applied, PU = prills, GU = granule, USG = super granule, UI = urease inhibitor, UNI = combined urease plus nitrification inhibitors. $LSD_{0.05}$ = least significance difference at 5% level (after Khalil *et al.* 2009b)

Under laboratory conditions, the relative loss of N_2O from either urea granule size amended with the NI and UNI (a new combined inhibitor) was small (0.08-0.14%) (Khalil *et al.* 2009c). They also found that the soil mixed NI and UNI reduced N_2O by 13-20% over broadcasting method, relating either to delayed nitrification resulting in immobilization or to enhanced NH_3 volatilization in presence of NI. The NI alone either as DCD or DMPP variably decreased N_2O emission, ranging from 20-53% under wheat and barley (Linzmeier *et al.* 2001; Mojumdar *et al.* 2002; Boeckx *et al.* 2005), and even up to 60% reduction with the DCD/TZ (Weber *et al.* 2004). However, application of NI was omitted under cropped conditions due to similar response as to UNI observed. Overall, the soil mixed UI and UNI reduced N_2O emission by 23-31% over the PU and by 47-52% over the same granule size. Though smaller compared to ours, a reduction of N_2O with the DCD + HQ-amended urea by 25.1% (Boeckx *et al.* 2005) was in evidence. The USG retained more mineral N than the urea amended with inhibitors (Tenuta and Beauchamp 2000; Khalil *et al.* 2006), more (7 weeks) than the inhibitors (5 weeks) but effective, as observed with the NI by Weber et al. (2004). Its affectivity could last even up to 4-8 weeks using DCD or DMPP (Linzmeier *et al.* 2001; Majumdar *et al.* 2002). The difference in this research was probably due to the higher mobility of inhibitors, the type of N fertilizer, and the temperature differences in particular. Under cropped conditions, N_2O emission was small particularly with the UNI, attributing to the controlled soil water conditions and the low N rate and the contribution of nitrification more, following degradation of DCD + TZ, than denitrification.

Conclusions

The relatively larger urea granule (USG) appeared to be more practical and efficient in reducing NH_3 and NO_x losses and delayed nitrification more as compared with the mixing of PU and urease inhibitor. The USG approach could increase somewhat N_2O emissions but the reduction potential is more than double over the IPCC default emission factor. Importantly, this can secure N supply at a later plant growth by delaying nitrification and gaseous N losses, similar to urease and nitrification inhibitors, over the PU. Surface application of UI could enhance N_2O emission more than the soil mixing approach. Though the NI responded similarly to reduce N_2O emissions, the UNI could reduce urea-induced NH_3, NO_x and N_2O losses following either mixing or broadcasting methods but adjustment of timing for fertilisation would be required.

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