N$_2$O, NH$_3$ AND NO$_x$ EMISSIONS AS A FUNCTION OF UREA GRANULE SIZE AND SOIL TYPE UNDER AEROBIC CONDITIONS

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Abstract. We examined the influence of various urea granule sizes (<2, 7.0, 9.9 and 12.7 mm) applied into a silt loam soil (experiment 1) and soil types (sandy, silt and clay loam) treated with the largest granule (experiment 2) on gaseous N loss (except N$_2$) at field capacity. The prilled urea (PU) was mixed into the soil whereas the urea granules were point-placed at a 5.0-cm depth. For experiment 1, N$_2$O emission was enhanced with increasing granule size, ranging from 0.17–0.50% of the added N during the 45-day incubation period. In the case of experiment 2, the sandy loam soil (0.59%) behaved similarly with the silt loam (0.53%) but both showed remarkably lower emissions than were found for the clay loam soil (2.61%). Both nitrification and N$_2$O emissions were delayed by several days with increasing granule size, and the latter was influenced by mineral N, soil water and pH. By contrast, the NH$_3$ volatilization decreased with increasing granule size, implying the inhibition of urease activity by urea concentration gradients. Considering both experimental results, the NH$_3$ loss was highest for the PU-treated (1.73%) and the larger granules regardless of soil type did not emit more than 0.27% of the added N over 22 days, possibly because the high concentrations of either mineral N or NH$_4^+$ in the soil surface layer (0–2.5 cm) and the high H$^+$ buffering capacity might regulate the NH$_3$ emission. Similar to the pattern of NH$_3$ loss, NO$_x$ emission was noticeably higher for the PU-treated soil (0.97%) than for the larger granule sizes (0.09–0.29%), which were the highest for the sandy and clay loam soils. Positional differences in the concentration of mineral N and nitrification also influenced the NO$_x$ emission. As such, total NH$_3$ loss was proportional to total NO$_x$ emission, indicating similar influence of soil and environmental conditions on both. Pooled total N$_2$O, NH$_3$ and NO$_x$ emission data suggest that the PU-treated soil could induce greater gaseous N loss over larger urea granules, largely in the form of NH$_3$ and NO$_x$ emissions, whereas a similar increase with the largest granule size was mainly due to the total N$_2$O flux.

Keywords: field capacity, gaseous N emission, N transformation, soil type, agricultural fertilizer

1. Introduction

Nitrous oxide (N$_2$O), ammonia (NH$_3$) and nitrogen oxides (NO$_x$) are interrelated through their emissions in global N cycling. Application of nitrogenous fertilizers for agricultural production is responsible for the major share of the gaseous N species released to the atmosphere. Anthropogenic activities have been responsible for the annual increases in N$_2$O emissions over the past decade (Sowers, 2001),

contributing to the greenhouse effect and ozone layer depletion. Agriculture is the primary source of NH_3 and the deposition of NH_3 together with NO_x (NO and NO_2) to the terrestrial and aquatic systems causes an increase in soil acidity, eutrophication and a decrease in biodiversity (Crutzen, 1979; Schulze *et al.*, 1989). NO_x is also both directly and indirectly contributing to global warming and ozone depletion, by controlling the tropospheric and stratospheric chemistry. NO_x concentrations depend on the proximity of their sources because of their short atmospheric lifetime, with anthropogenic sources exceeding natural ones (e.g., lightning and microbial activity in soils), which represent only 30% of the total emissions (Delmas *et al.*, 1997).

The formation of N_2O is mostly biogenic and occurs simultaneously through both denitrification and nitrification processes, with the dominant process depending on the availability and type of substrates and on soil water regimes (Khalil *et al.*, 2002a; Khalil and Baggs, 2005). N_2O emissions from agricultural land vary from 0.03 to 2.7% (Eichner, 1990) and can even reach up to 5.8% (Dobbie *et al.*, 1999) of the added N. The redistribution of other N losses such as N runoff, leached NO_3^-, NO_x and NH_3 emissions can also result in indirect N_2O release (Mosier *et al.*, 1998; Smith *et al.*, 1998). It is estimated that 23% of global NH_3 emission is derived from fertilizers and field-applied manure (Bouwman *et al.*, 2002); the proportion of its loss from N fertilizers can range from ≈ 0 to >50% depending on fertilizer type, soil and environmental conditions (Sommer *et al.*, 2004). The available information on the formation process of nitric oxide (NO) or NO_x is conflicting, with during both nitrification and denitrification (Firestone and Davidson, 1989) or exclusively during nitrification (Russow *et al.*, 2000). It is estimated that the increasing use of N fertilizers in agriculture will account for >50% of the global NO_x budget by 2025 (Yienger and Levy II, 1995).

Globally, urea is the cheapest and mostly used commercial inorganic N fertilizer for agricultural production. Both broadcasted and top-dressed prilled urea (PU) and deep-placed (4 cm) urea super granule (USG) in coarse-textured soils are prone to NH_3 volatilization (Buresh, 1987; Sommer *et al.*, 2004). Mixing urea with soils, a banded/deep placement, immediate rainfall/irrigation and rapid drying of the surface soil after application might reduce these same losses (Bouwmeester *et al.*, 1985; Weber *et al.*, 2000; Khalil *et al.*, 2005) depending on the soil type and water transmission. As an alkaline-hydrolyzing N fertilizer, urea influences nitrification through a transient rise in pH with subsequent denitrification leading to the formation and release of large amounts of N_2O (Mulvaney *et al.*, 1997; Khalil *et al.*, 2002b). In the zone of USG placement, a high-localized urea/NH_4^+ concentration develops followed by an increase in soil pH through enzyme-catalysed hydrolysis (Singh *et al.*, 1994). However, dissolution of deep-placed USG occurs slowly and inhibits both urease and nitrifier activity, and molecular diffusion is likely the predominant mechanism for the movement of dissolved urea (Shah and Wolfe, 2003). Tenuta and Beauchamp (2000) showed that use of USG increased N_2O production to a maximum of 1.24% of the added urea-N, with the presence of NO_2^- being the

dominant factor influencing its release. High NH$_4^+$ concentrations could also facilitate NO$_x$ emissions under aerobic conditions (Russow *et al.*, 2000). Diffusion and mass flows of the concentrated NH$_4^+$ that develop within a USG placement zone are thought to link with different soil and environmental factors to influence N$_2$O and other gaseous N losses. However, both the soil type and depth of placement might also regulate the processes through the degree of antecedent cation exchange sites.

Deeper placement of USG is technologically and agroeconomically advantageous in improving N use efficiency in lowland rice fields (Savant and Stangel, 1990; Mohanty *et al.*, 1999). This technology might be effective agronomically for up/dryland cropping systems (Mohanty *et al.*, 1999; Haque, 2002), but uncertainty prevails with regard to the environmental consequences. High NH$_3$ volatilization from sandy and N$_2$O emission from silt loam soils treated with USG have been reported (Buresh, 1987; Tenuta and Beauchamp, 2000). Further interest in the emission potentials of gaseous N species from agricultural soils treated with USG to the atmosphere, their interactions and possible environmental consequences has called for technological decision supports. Thus, we carried out experiments (a) to investigate the influence of various urea granule sizes on N$_2$O, NH$_3$ and NO$_x$ emissions from a silt loam soil, (b) to determine the role of contrasting soil types with point-placed USG on N$_2$O, NH$_3$ and NO$_x$ emissions, and (c) to elucidate the interrelations between the gaseous N species over time and the factors affecting their emissions.

2. Materials and methods

2.1. SOIL CHARACTERISTICS

Field-moist soils were collected up to a 15-cm depth from three different locations to represent contrasting soil types, and passed through a 5-mm mesh sieve and stored in a dark, cool (4–5 °C) place. The soil collected from the Dürnast experimental farm of the Technical University of Munich, Freising, Germany was a loess silt loam. The two other soils, sandy loam and clay loam, were collected from the Scheyern experimental station of GSF-National Research Centre for Environment and Health, Germany. Some physical and chemical properties of these soils are presented in Table I. Two separate experiments were conducted using pots 0.20 m × 0.22 m in size for N$_2$O and CO$_2$ measurements. Each pot was filled with 6 kg of dry soil. NH$_3$ and NO$_x$ emission was studied separately using PVC rings with a sealed bottom (0.13 m × 0.12 m) receiving 1.5 kg of dry soil. The soils were watered to field capacity [−10 kPa for sandy loam (0.21 kg H$_2$O kg^{-1}) and −33 kPa for both silt loam (0.27 kg H$_2$O kg^{-1}) and clay (0.32 kg H$_2$O kg^{-1} oven-dry soil] and water lost during the incubation period was replaced every three days.

TABLE I

Some physical and chemical properties of the experimental soils

Soils (USDA Taxonomy)*	Land use	Particle size distribution (%)			Texture	pH	Organic C (%)	Total N (%)	C/N	CEC (cmol$_c$ kg^{-1} soil)
		Sand	Silt	Clay						
1. Loamy-skeletal (Typic Udorhent)	Cereal-potato	60	29	11	Sandy Loam	5.2	1.25	0.14	9.3	10.8
2. Fine silty (Dystric Eutrochrept)	Legume grass (mixture)	20	60	20	Silt loam	6.4	1.61	0.17	9.5	17.6
3. Fine loamy (Dystric Eutrochrept)	Legume-cereal-potato	26	46	28	Clay loam	5.9	1.84	0.20	9.4	23.2

*Sinowski and Auerswald (1999).

2.2. Experiment 1: Effect of urea size on gaseous N and C loss

This experiment was designed to investigate the influence of various urea granule sizes at field capacity. Urea fertilizer was applied to the pots (area of $\sim$0.0127 m^2) filled with the silt loam soil and thereafter watered to the desired level. Incubation was carried out at air temperature of $20 \pm 2\,^\circ$C. The treatments were N$_0$ – unfertilised control, PU – prilled urea ($<$2 mm dia.), USGs- urea super granule, USG (small = 7.0 mm; 0.25 g), USGm - USG (medium = 9.9 mm; 0.50 g) and USGl - USG (large = 12.7 mm; 1.0 g). The PU was mixed into the soil and the USG was point-placed at a soil depth of 5 cm. Each treatment consisted of three replicates. The urea-N rate was 363 kg N ha^{-1} (181 mg N kg^{-1} soil).

2.3. Experiment 2: Effect of soil type on gaseous N and C loss with point-placed USG

In this experiment, emphasis was given on determining the effect of contrasting soils with the USGl (sandy loam, USG-SL; silt loam, USG-SiL: and clay loam, USG-CL) at point-placed 5-cm soil depth. An unfertilised control for each soil was also used. Watering was done after fertilization to reach the respective field capacity. The experimental conditions were similar to experiment 1 except that the N rate was 366 kg N ha^{-1} (182 mg N kg^{-1} soil).

2.4. Gas sampling and measurement of N$_2$O and CO$_2$

Gas was collected in triplicate using a ventilated closed chamber (area 0.0109 m^2; vol. 1.66 l) to measure N$_2$O and CO$_2$ concentrations at days 1, 3, 6, 9, 12, 16, 20, 25, 30, 37 and 45. Using an airtight syringe, 20 ml of gas was collected from the headspace and injected into a pre-evacuated 12 ml serum tube fitted with butyl rubber stoppers. The gas was sampled at 0, 20 and 40 min between 11:00 and 12:00 h and analysed within one week using an automated gas chromatograph (Varian Star 3400, USA) equipped with electron capture and thermal conductivity detectors. 'Star Chemstation' was used to measure the concentrations of the gases.

2.5. NH$_3$ and NO$_x$ measurement

As mentioned above, a separate experiment was conducted for all the treatments in experiments 1 and 2 to measure NH$_3$ and NO$_x$ emissions over 22 days, where background emissions were considered to be the control. The PVC rings (four in each chamber) were filled with soil as per the treatments and placed inside a dynamic chamber (area 0.125 m^2, dia 0.40 m, height 0.40 m). Each chamber was covered with acrylic glass that was fitted with a stainless steel ring and placed on a long tray filled with sand to measure gas fluxes over time. This method can measure

both NH_3 and NO_x simultaneously by flowing the sample air to a two-channel chemiluminescence NO-Analyser (CLD 700AL, Fa. EcoPhysics, Gürnten, CH). The whole measurement system has six parallel chambers with a continuous airflow (ca. 40 L/min) and continuous gas sampling flow (4 L/min) that are controlled by a mass-flow controller (Fa. Qualiflow, France). The computer software (NEMO, Schmidt Institute, Germany) both controls the gas sampling system and has a data-saving facility for the gases and the airflow measurements.

2.6. SOIL ANALYSIS

Soil was sampled from additional treatment pots using a large auger-like stainless tube (area $\sim 0.0127\,m^2$) at days 1, 9, 25 and 45. At the end of NH_3/NO_x study (22 days), soils were sampled from 0 to 2.5 cm and 2.5 to 10 cm depths. After thorough mixing, a sub-sample of 100 g was extracted with 1 M KCl at a soil:KCl solution ratio of 1:2.5 to determine NH_4^+-N colorimetrically via the salicylate method (Keeney and Nelson, 1982) using a UV/VIS Spectrometer (Parkin Elmer, Lambda 20). Another sub-sample of 100 g was extracted with 0.01 M $CaCl_2$ at a soil:$CaCl_2$ solution ratio of 1:2.5 to determine both NO_3^-- and NO_2^--N contents using HPLC (UVIKON 720LC, Shimadzu C-R3A Chromatopac; Vilsmeier, 1984). The latter extract was also used to measure soil pH.

2.7. STATISTICAL ANALYSIS

Statistical analysis was performed using the computer package JMP v4.0.2 of SAS Inc. An ANOVA at a probability level of 5% was used to test the significance of the treatment effects. Total N_2O and CO_2 emissions were calculated by integrating the area of the daily fluxes. The sum of the daily fluxes for NH_3 and NO_x were taken to represent total emissions. The day at which 50% of the total fluxes ($t_{\frac{1}{2}}$) occurred was identified. Relative loss of the added N was calculated based on total N_2O, NH_3 and NO_x fluxes under control or background emissions. Regression analyses were performed to identify any constant relationship between N_2O as the independent variable and soil properties (including CO_2) as dependent variables and any interrelation between the gaseous N species.

3. Results

3.1. EXPERIMENT 1: EFFECT OF UREA SIZE ON GASEOUS N AND C LOSS

The silt loam soil received an equal amount of urea-N with respect to surface area regardless of whether it was treated with PU or urea of various granule sizes. The maximum peaks for N_2O emissions were attained progressively earlier with decreasing granule size (Figure 1a).During the 45 days of the incubation, the total fluxes were
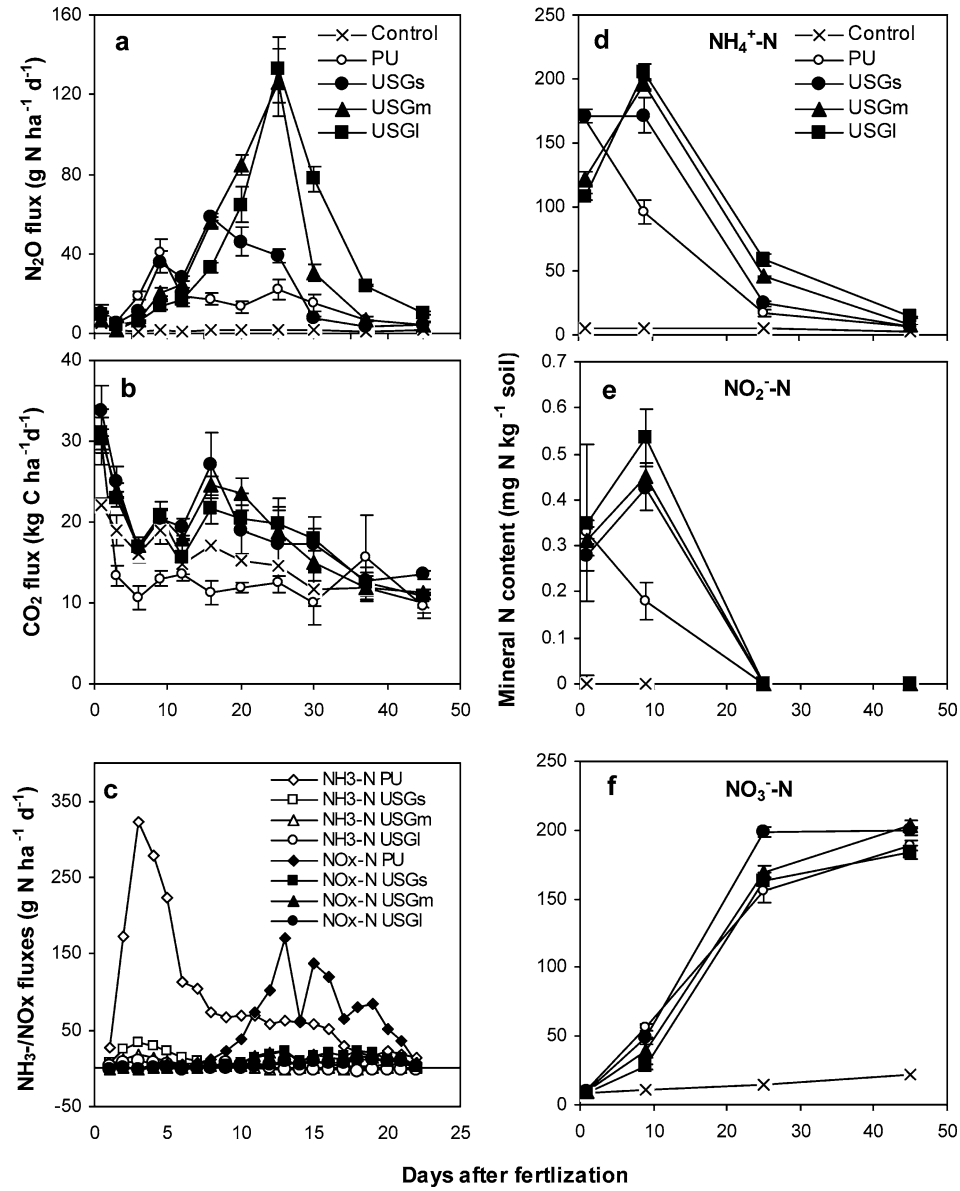
Figure 1. Gaseous N (a, c) and CO$_2$ (b) emissions and changes in mineral N (d, e, and f) in a silt loam soil treated with various urea granule size [PU = prilled urea; USGs = urea super granule (small = dia. 7.0 mm); USGm = urea super granule (medium = 9.9 mm); USGl = urea super granule (large = 12.7 mm)]. Vertical bars indicate standard errors.

TABLE II

Total N_2O, CO_2, NH_3 and NO_x fluxes and relative gaseous loss of the added N during the 45-day incubation period (22 for NH_3 and NO_x) as influenced by urea granule size and soil type

Treatments	Total emission (g N ha^{-1})				Relative loss of added N (%)			Gaseous N loss (%)
	N_2O	CO_2	NH_3	NO_x	N_2O	NH_3	NO_x	
Experiment 1 (Urea granule size)								
Control	68.9	656.9						
PU	675.9	589.1	1929.7	1084.9	0.17	1.73	0.97	2.87
USGs	992.1	842.2	218.7	213.1	0.25	0.20	0.19	0.64
USGm	1671.3	817.9	75.6	177.2	0.44	0.07	0.16	0.67
USGl	1916.7	807.8	39.9	95.0	0.50	0.04	0.09	0.63
LSD$_{0.05}$	518.8	152.2			0.17			
Experiment 2 (Soil type!)								
Control- SL	665.9	525.3						
Control-SiL	87.0	571.7						
Control-CL	1732.8	810.4						
USG-SL	2791.1	805.6	297.9	232.5	0.59	0.27	0.21	1.07
USG- SiL	2017.5	656.0	39.9	95.0	0.53	0.04	0.09	0.66
USG- CL	11218.6	926.9	272.8	325.2	2.61	0.25	0.29	3.15
LSD$_{0.05}$	903.4	133.0			0.16			

*CO_2 = kg C ha^{-1}, PU = prilled urea, USGs, m, l = urea super granule size [s = small (dia. 7 mm); m = medium (9.9 mm); l = large (dia. 12.7 mm)]; SL = sandy loam, SiL = silt loam, CL = clay loam; LSD$_{0.05}$ = least significant difference at 5% level; ! = treated with the USGl.

enhanced with increasing granule size and the relative loss of the added N ranged from 0.17–0.50% although the two neighbouring sizes responded identically (Table II). The point at which 50% of total N_2O fluxes ($t_{\frac{1}{2}}$) occurred was delayed between 1 and 9 days with the larger granule sizes as compared to the PU. The CO_2 evolution rose in the beginning of the experiment with the larger granules demonstrating smaller secondary peaks at day 16 (Figure 1b). CO_2 fluxes did not differ significantly between the larger granules, which values were significantly higher than those with PU. As such, its total flux did not vary significantly between the larger sizes (Table II).

The NH_3 volatilization was highest from the PU-treated soil, peaked at day 3 (323.2 g N ha^{-1} d^{-1}) and decreased over time with increasing granule size (Figure 1c). For the USG treatments, the USGs showed the highest peak (33.4 g N ha^{-1} d^{-1}). The trends for total NH_3 loss over the 22 days followed the peaked emissions, with the relative loss of the added N ranged from 0.04–1.73% (Table II). The NO_x emissions started to increase while NH_3 volatilization was declining, with the peaks for the former showing trends that were similar to the latter. The relative loss of added N as NO_x was highest for the PU treatment (0.97%) and treat-

ments with the larger USG demonstrated about two-fold higher emissions for NO$_x$ (0.09–0.19%) than for NH$_3$. Overall, the relative gaseous N loss (N$_2$O + NH$_3$ + NO$_x$) of the added N was several-fold higher for the PU than for the larger granules.

Accumulation and disappearance of NH$_4^+$-N over time was delayed with increasing granule size (Figure 1d). The two largest granules displayed peaks for NH$_4^+$-N at day 9 (197–205 mg N kg^{-1} soil) and afterwards, the USGl treatment showed significantly higher than that of the other treatments. The trends for NO$_2^-$-N were similar to those of NH$_4^+$-N but the overall concentration was low (<0.54 mg N kg^{-1} soil), presumably due to the mixing of the large soil volumes needed to prepare the extracts, and it was not traceable from day 25 onwards (Figure 1e). By contrast, the NO$_3^-$-N accumulation was rapid until day 25 of the incubation and the larger granules delayed nitrification significantly (Figure 1f). Soil pH decreased over time, with the decrease appearing earlier for the smaller granules (data not shown). Net N mineralization in 45 days over the control value was significantly higher throughout for the larger granules (Figure 2a).It decreased slowly from its peak at day 9 (104.6–117.4 mg N kg^{-1} soil), with the PU treatment having negative values recovering over time. By contrast, net nitrification was significantly lower in the larger granules at day 9 and became dominant in the N mineralization process. At day 45, net nitrification was identical between the PU and USGl treatments (174.6–176.6 mg N kg^{-1} soil), which were significantly lower than the others (189.7–194.2). In the case of the NH$_3$ and NO$_x$ study, the concentration gradients of mineral N differed between urea granule sizes, but were higher in the 0–2.5 cm than at a 2.5–10 cm soil depth (Figure 2b).

3.2. EXPERIMENT 2: EFFECT OF SOIL TYPE ON GASEOUS N AND C LOSS WITH POINT-PLACED USG

The maximum peaks for N$_2$O emissions from the sandy and clay loam soils treated with the large USG (USG-SL and -CL) were attained by day 3 (330.1 versus 526.5 g N ha^{-1} d^{-1}; Figure 3a).The response difference between the control and USG treatments was small for the latter soil. The N$_2$O emission from the USG-CL increased almost exponentially after day 12, with similar high peaks at day 25 and 30 before decreasing quickly afterwards. As such, the total N$_2$O flux or loss of the added N was 6–8 times higher in the USG-CL over the other two soils, with the value in the -SL being 10% higher than that for the -SiL (Table II). The t$_{\frac{1}{2}}$ occurred was delayed by 17–24 days over the respective control treatments, and more so for the USG-CL. The trends for rates of CO$_2$ evolution were similar to those of the N$_2$O fluxes. An exception was for the USG-CL initially, where the third largest peak appeared at day 9, but was smaller than that from the -SL (Figure 3b). Thus, the total CO$_2$ evolution was higher from the USG-CL although statistically similar to -SL (805.6–926.9 kg C ha^{-1}). However, the USG-SL demonstrated a significantly greater N-induced total CO$_2$ emissions of 280.3 kg C ha^{-1} as
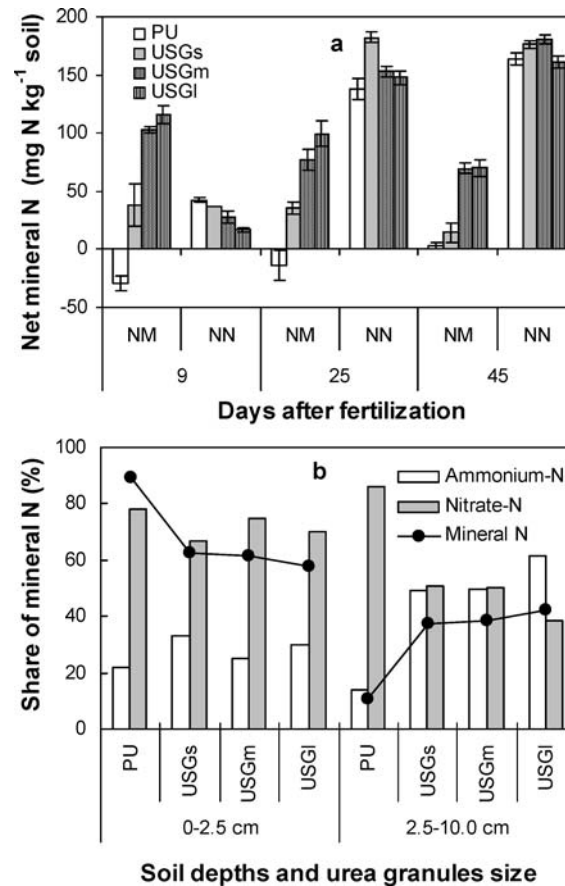
Figure 2. Net N mineralization (NM) and nitrification (NN) over 45 days (a) and NH_4^+- and NO_3^--N both individually and combined at the end of NH_3 and NO_x study (22 days) in the surface and sub-surface layers (b) as influenced by urea granule size [PU = prilled urea; USGs = urea super granule (small = dia. 7.0 mm); USGm = urea super granule (medium = 9.9 mm); USGl = urea super granule (large = 12.7 mm)].

compared to 81.0–116.5 kg C ha^{-1} for the other two soils (with USG-SiL having the lower value).

The NH_3 volatilization from the USG-SL peaked at day 8 (46.7 g N ha^{-1} d^{-1}) and decreased rapidly afterwards (Figure 3c). Two short peaks appeared for the USG-SiL during the study period, the highest being at day 3 (10.2 g N ha^{-1} d^{-1}), and NH_3 consumption was observed from day 13 onwards. The USG-CL showed a maximum peak at day 9 only (42.6 g N ha^{-1} d^{-1}). The total NH_3 loss was highest from the USG-SL, followed by the -CL and then the -SiL, ranging from 0.04–0.27% (Table III). As in experiment 1, the maximum peaks for NO_x were attained two days earlier for both the USG-SL and -SiL than for the -CL (Figure 3c). The total NO_x
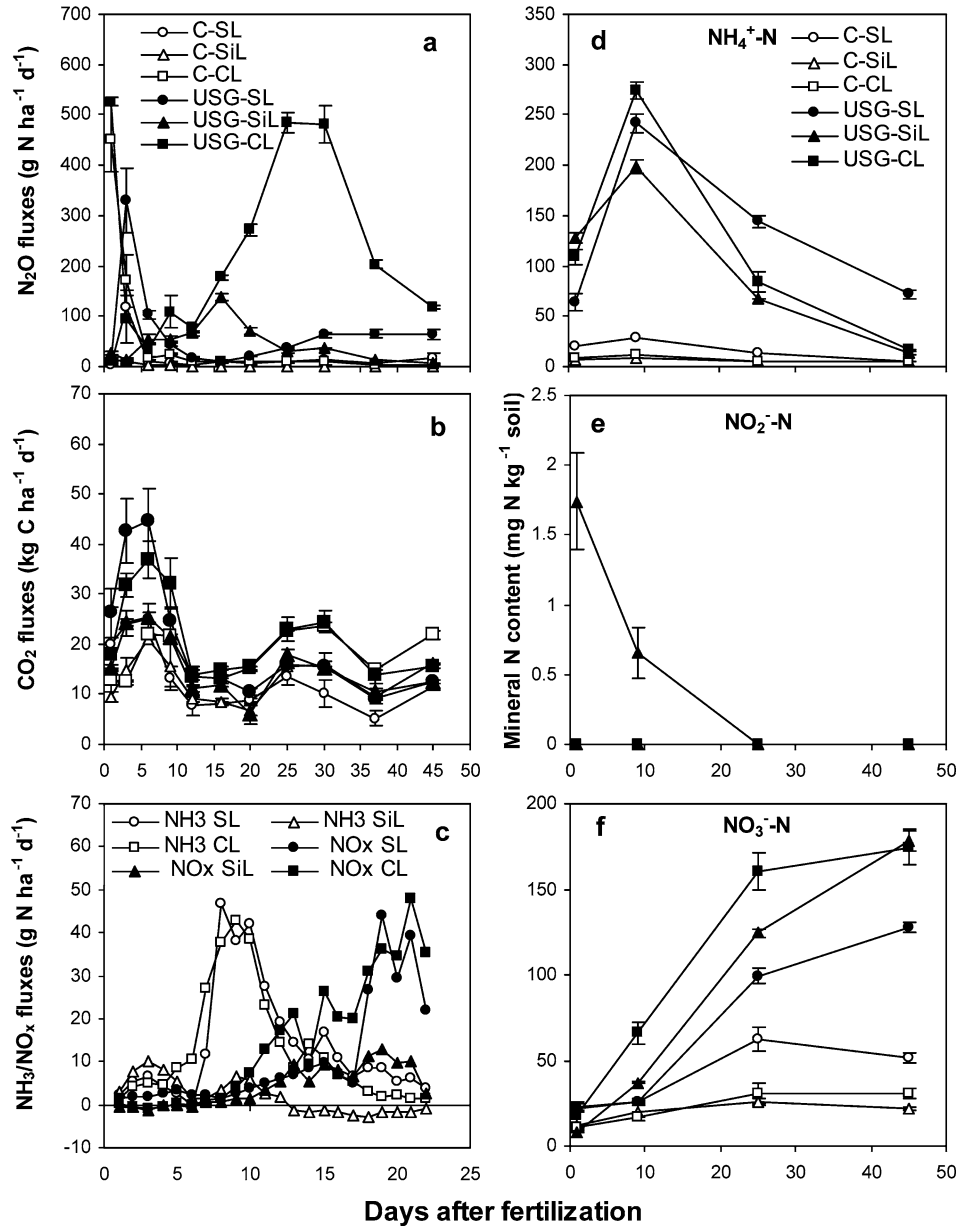
Figure 3. Gaseous N (a, c) and CO_2 (b) emissions and changes in mineral N (d, e, and f) in three contrasting soils treated with the large (dia. 12.7 mm) urea super granule, USG (C = control; SL = sandy loam; SiL = silt loam; CL = clay loam). Vertical bars indicate standard errors.

TABLE III

Correlation coefficients of N_2O fluxes ($\log_e$-transformed, mean values) with soil variables as influenced by urea granule size and soil type

	Urea granule size		Soil type with USG	
Variables	Simple linear regression	Regression coefficients (Multiple, stepwise)	Simple linear regression	Regression coefficients (Multiple, stepwise)
CO_2	−0.15	N_2O (ln) =	0.03	N_2O (ln) =
ln-CO_2	−0.11	$-10.711 + 0.017 \times NO_3^-$	0.03	$4.885 + 0.016 \times NH_4^+$ -
NH_4^+-N	−0.01	$+ 0.009 \times NH_4^+ + 0.178$	0.21*	$1.161 \times pH + 0.059$
NO_3^--N	0.55***	$\times$ WFPS	0.08	$\times$ WFPS
NO_2^--N	−0.04		0.01	
PH	−0.25*	$R^2 = 0.70, P < 0.001,$	−0.01	$R^2 = 0.54, P < 0.01,$
WFPS	0.06	$n = 20$	0.10	$n = 24$

*, **, *** indicate significance at $P < 0.05$, 0.01, 0.001, respectively.
ln-CO_2, $\log_e$-transformed CO_2; ln-N_2O, $\log_e$-transformed N_2O; USG, urea super granule; WFPS, water-filled pore space (N_2O = g N ha^{-1} d^{-1}, CO_2 = kg C ha^{-1} d^{-1}, Mineral N = mg N kg^{-1} soil, WFPS =%).

emission was higher for the USG-CL and -SL, with the relative loss of the added N ranged from 0.09–0.29% (Table II). Thus, gaseous loss ($N_2O + NH_3 + NO_x$) of the added N was several-fold higher from the USG-CL than for the -SL and -SiL.

Accumulation of NH_4^+-N until day 9 of the incubation was faster in the USG-CL and -SL than in the USG-SiL (Figure 3d), with the respective concentrations being 274, 242 and 212 mg N kg^{-1} soil. Afterwards, NH_4^+-N concentrations were reduced sharply in the USG-CL and -SiL contrasting to the -SL. As in experiment 1, the NO_2^--N concentration was traceable in only the USG-SiL and only before day 25, the highest occurring at day 1 (1.74 mg N kg^{-1} soil; Figure 3e). Following the trends of NH_4^+-N disappearance, NO_3^--N accumulation was significantly higher in the USG-CL (161 mg N kg^{-1} soil) than for the other two soils (99–125; Figure 3f), which showed identical differences at the end of the study. The changes in soil pH over time largely followed the nitrification process (data not shown). Net N mineralization was significantly higher at day 9 in the USG-CL and -SL (208 and 169 mg N kg^{-1} soil, respectively) than in the -SiL (102; Figure 4a). Afterwards, the USG-SL showed significantly higher net mineralization. By contrast, net nitrification was significantly lower for the USG-SL throughout (0.70–77 mg N kg^{-1} soil). The USG-CL and -SiL, however, showed little changes in net nitrification from day 25 onwards (114–160 mg N kg^{-1} soil) as the presence of NH_4^+-N to be nitrified was small. At the end of NH_3 and NO_x study, the concentrations of mineral N in the USG-SiL and -CL were higher at the 0–2.5 cm than at a 2.5–10 cm soil depth and it differed marginally for the -SL (Figure 4b).
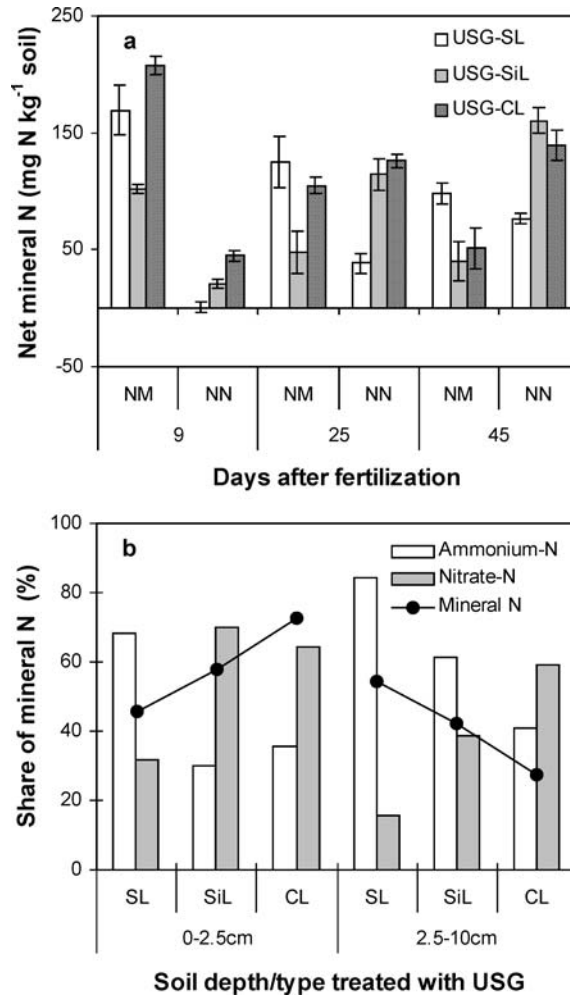
Figure 4. Net N mineralization (NM) and nitrification (NN) over time (a) and share of NH_4^+- and NO_3^--N both individually and combined at the end of NH_3 and NO_x study (22 days) in the surface and sub-surface layers (b) as influenced by soil type treated with the large (dia. 12.7 mm) urea super granule, USG (SL = sandy loam, SiL = silt loam; CL = clay loam). Vertical bars indicate standard errors.

3.3. RELATIONSHIPS

For experiment 1, the $\log_e$-transformed N₂O fluxes (ln-N₂O) showed a significant positive relationship with NO_3^--N and a significant negative relationship with pH (Table III). Multiple stepwise regression analysis depicted a best fit for ln-N₂O fluxes with NO_3^--N, NH_4^+-N and WFPS ($R^2 = 0.70$, $P < 0.001$, $n = 20$). For experiment 2, the only significant relationship observed between the raw or

ln-N_2O fluxes and the individual soil variables was for NH_4^+-N ($R^2 = 0.21$ $P < 0.05$). However, the ln-N_2O fluxes showed a significant positive relationship with NH_4^+-N and WFPS and a negative one with pH ($R^2 = 0.54$, $P < 0.01$, $n = 24$). Irrespective of urea granule size and soil type, the ln-N_2O flux was predicted well (56%) with the combination of NO_3^--N, NH_4^+-N, WFPS and pH (Figure 5a).

For experiment 1, surface mineral N (% share/total) was highly related to the sum of NH_3 and NO_x emissions ($R^2 = 0.97$–0.99, $P < 0.05$–0.01), and total NO_3^--N with the latter ($R^2 = 0.93$, $P < 0.05$), linking to the presence of NH_4^+-N as well that was nitrified during the study period. For experiment 2, no significant relationships between the sum of NH_3 and NO_x emissions and mineral N in the soil surface layer were observed. However, a good relationship was found when total NH_4^+-N in surface layer, which showed lower overall emissions than
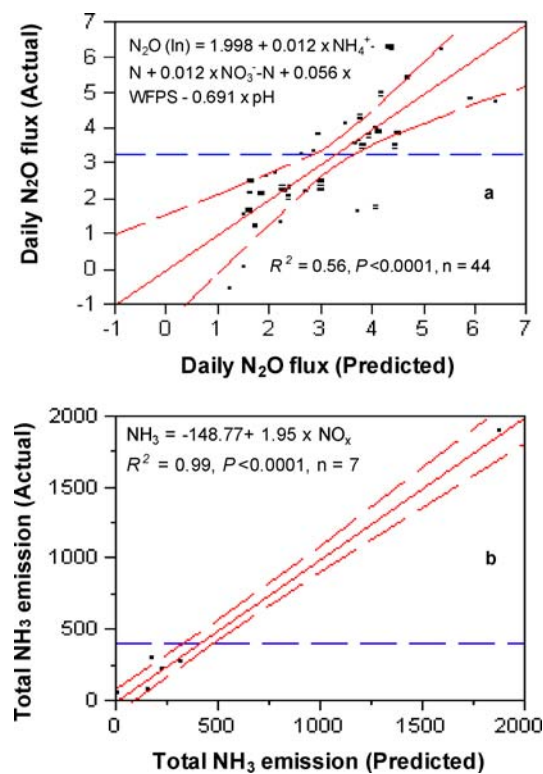

Figure 5. Actual and predicted N_2O (ln) fluxes (g N ha^{-1} d^{-1}) during the 45-day incubation period (a) and total NH_3 volatilization in relation to total NO_x emission (g N ha^{-1}) during the 22-day study period (b) irrespective of urea granule size and soil type. Corresponding soil factors influencing emission and their regression equations are shown, with the coefficients of determination, (NH_4^+-N & NO_3^--N = mg N kg^{-1} soil; water-filled pore space, WFPS = %).

NH$_3$ and NO$_x$, was taken as the dependent variable ($R^2 = 0.99$, $P < 0.07$, $n = 3$). The relationship between total N$_2$O and either NH$_3$ or NO$_x$ emissions was poor. However, the total NH$_3$ lost was significantly related to the NO$_x$ emissions (Figure 5b).

4. Discussion

4.1. N$_2$O EMISSIONS WITH UREA SIZE AND SOIL TYPE

The N$_2$O emission was enhanced with increasing urea granule size, when either PU was mixed into a silt loam soil or USG were point-placed into it at 5.0-cm depth (experiment 1). Similar and higher N$_2$O emissions, either with the PU or large USG (0.17–0.56%: up to 1.24%) and a USG-induced delay of several days in its emission potential in a silt loam soil have also been reported (Tenuta and Beauchamp, 2000; Khalil *et al.*, 2005). However, we found that the delay in reaching 50% emission varied with urea granule size and soil type, with the day of occurrence of the larger peaks appearing during the study periods. When USG was point-placed to the three contrasting soils (experiment 2), the N$_2$O loss of the added N from the USG-SiL was similar to that in experiment 1, although the maximum peaks were attained somewhat earlier. The USG-SL released a slightly higher amount of N$_2$O, whereas the control itself had several-fold larger N$_2$O emissions than the -SiL, indicating the influence of lower pHs towards increasing the mole fraction of N$_2$O during nitrification in the sandy loam soil (Mulvaney *et al.*, 1997; Van Cleemput, 1998; Khalil *et al.*, 2002b) as compared to the other two soils. The large loss from the clay loam soil (2.61%) might be attributable to the major contribution of the denitrification process, relating to high water-filled pore space (Khalil and Baggs, 2005).

The high concentration gradients of NH$_4^+$, NO$_2^-$ and pH might facilitate the increased N$_2$O emissions from the USG-treated soil, limiting nitrification for a considerable period. The presence or disappearance of NO$_2^-$ could regulate its formation and release (Tenuta and Beachamp, 2000; Khalil *et al.*, 2005). However, it can be formed through true or nitrifier denitrification (Bremner, 1997; Wrage *et al.*, 2004) or, when the soil pH is favourable, chemodenitrification (Van Cleemput, 1998). We could not trace NO$_2^-$ in the USG-SL or -CL, where either rapid reduction was occurring or it was consumed by the soil, given that it is unstable in acid soils (Van Cleemput, 1998). The differences among the soils also imply that soils having large priming effects (Kuzyakov *et al.*, 2000) might also enhance N$_2$O emission because soil N is generally the major source.

The relationship between N$_2$O and soil variables indicates that the formation and release of N$_2$O depended on the forms of mineral N that were present to be either nitrified or denitrified, coupled with the soil water content and soil pH. However,

soil pH might be dominant over the influence of CO_2 on N_2O emissions when contrasting soils are considered, and the impact of acidic soils for enhancing N_2O emissions has also been reported. Excluding soil pH, a similar relationship but together with CO_2 flux has been reported by Khalil *et al.* (2005); the impact of soil water is notably in agreement with those of others (Hosen *et al.*, 2002; Tenuta and Beauchamp, 2003). These findings point out that the stated soil variables under aerobic conditions could mask the influence of urea granule size and soil type, and even of N fertilizer type, under field conditions (Khalil *et al.*, 2002a) and thus, could reduce the uncertainty for estimation of N_2O emissions. Soil water content below field capacity and its depletion over time could further reduce N_2O emissions, where supplemental irrigation resulted in negligible enhancements in its release (Khalil *et al.*, 2005). Results suggest that the mixing of PU into the soil could reduce N_2O emissions to some extent compared to point-placed USG, but with the effects being soil specific (with USG-CL showing the most favourable results).

4.2. NH_3 VOLATILIZATION WITH UREA SIZE AND SOIL TYPE

In contrast to the pattern observed for N_2O emissions, NH_3 volatilization decreased with increasing granule size, with the PU-treated silt loam soil emitting several-fold higher levels than did the same soil treated with the larger urea granules. The percent amount of mineral N in the 0–2.5 cm soil surface layer over 2.5–10 cm (assuming: urea hydrolysis $\rightarrow NH_3 \uparrow \leftrightarrow NH_4^+ \rightarrow NO_3^-$ transformations over time) was by far the highest (90%) in the PU-treated soil. This could largely be explained by NH_3 volatilization being a surface-related process. As such, the loss of NH_3 would increase with the application of urea and ammonium-based fertilizers to the soil surface (Bouwmeester *et al.*, 1985), with intensive NH_4^+ accumulation through vapour diffusion from the sub-surface layer (Ferguson and Kissel, 1986) and/or during the formation of ammoniacal-N through rapid mineralization. However, it appears that proper mixing of the PU deeper into the soil might reduce the loss greatly to levels that are largely similar to those obtained from USG point-placed into a silt loam soil taking the equal urea-N rate on surface area basis (Khalil *et al.*, 2005) and/or banding of urea at a certain depth into consideration (Sommer *et al.*, 2004).

Little NH_3 was volatilized from the three contrasting soils with USG point-placed at 5.0-cm depth, with the lowest value being obtained from the silt loam soil (0.04%). The initially increased pH levels of the soils (particularly clay loam and silt loam) treated with the large USG decreased slowly over time, indicating that the soils had high H^+ buffering capacities (Ferguson *et al.*, 1984) and were generally not conducive to high NH_3 loss. However, the percent share of mineral N in the 0–2.5 cm surface layer among the three soils had an inconsistent influence on NH_3 losses. This observation could derive from the low pH of the sandy soil coupled with the higher mineral N in the deeper (2.5–10 cm) layer linking to the watering events that enhanced convection flow. In the case of the clay loam soil, the large

number of exchange sites coupled with the anaerobic situation presumably acted as a barrier for NH$_3$ diffusion compared to the pH level and N transformations found in the silt loam soil. Nevertheless, the likely molecular diffusion of mineral N over time from the placement zone of USG (Shah and Wolfe, 2003; Khalil *et al.*, 2005) and the limitation of urease activity imposed by high urea concentrations (Sommer *et al.*, 2004) might be advantageous in reducing NH$_3$ volatilization. Buresh (1987) reported that NH$_3$ volatilization was negatively correlated with soil clay content. In contrast to our finding of small NH$_3$ volatilization even from the sandy loam soil, he reported a large NH$_3$ loss (up to 67%, with variation in some soils of 2.9–4.1%) from 1.1 g of USG point-placed at 4 cm into several coarse textured soils. Possible reasons for the different findings could include the shallower placement, larger sand content, and lower H$^+$ buffering capacity and low carbon content in the soils examined by Buresh.

Our results indicate that mixing PU into the soil at a depth of 5.0-cm or more could greatly reduce NH$_3$ volatilization compared to the broadcasting method, as has also been reported by others (Weber *et al.*, 2001; Sommer *et al.*, 2004; Wang *et al.*, 2004). Point-placed large USG could also decrease NH$_3$ volatilization but the effect is soil-specific, in agreement with the results of Patel *et al.* (1989) who found that 1.47–3.07% was lost from an upland system. Soils having high H$^+$ buffering capacities might prevail over the high concentration gradients of NH$_4{}^+$ and pH, which occur in the placement zone only (Khalil *et al.*, 2005), leading to the fixation of NH$_3$ vapour within the upper soil. However, this result is presumably subject to receiving either controlled irrigation (preferably after fertilization) or small rainfall events (Bouwmeester *et al.*, 1985). By contrast, intensive and large irrigation events may cause hydrodynamic dispersion of mineral N to depths below the levels of the roots, causing groundwater pollution and reducing agroeconomic benefits.

4.3. NO$_x$ EMISSIONS WITH UREA SIZE AND SOIL TYPE

Similar to NH$_3$ volatilization, NO$_x$ emission increased with decreasing urea granule size. The PU mixed into the soil released several-fold greater levels of NO$_x$ compared to the other granule sizes. Hou and Tsuruta (2003) found similar percentages of NO-N loss when broadcasted urea was mixed to a 15-cm depth by ploughing down (∼0.78%) or band-placed at a 12-cm depth (∼0.03%, calculated). However, NO$_x$ emissions were lower than that reported with broadcasted urea (1.5%) by Weber *et al.* (2001). Similarly, its emission was also small from the USG-SL and -CL, but considerably higher than from the -SiL. This indicates that NO$_x$ emission is soil-specific and was probably limited by the presence of solution and gas phase in the respective soils (Skiba *et al.*, 1997) or that soil consumption was occurring (Hou and Tsuruta, 2003).

The positional differences in mineral N concentrations, as was the case for NH$_3$ loss, also support the trends for NO$_x$ emission. The delayed nitrification with

increasing urea granule size implies that nitrification was primarily responsible for NO_x production and release under aerobic conditions, in agreement with the findings of many researchers (Russow *et al.*, 2000; Zheng *et al.*, 2003). The presence of comparatively more NH_4^+ in the surface compared to sub-surface layers for subsequent nitrification could possibly influence NO_x emission for the sandy and clay loam soils (Hutchinson and Brams, 1992) so long as intraspecific soil moisture differences do not limit the process. A relatively higher emission from the clay loam soil could also be partially ascribed to the contribution of the reductive process whereby ammonia oxidizing bacteria use their product NO_2^- as an electron acceptor during O_2 limiting conditions (Remde and Conrad, 1990). It should be pointed out, however, that NO_x is typically not a major end product of N transformations in anaerobic soil systems (Remde *et al.*, 1989; Davidson, 1993). Furthermore, although the NO_x formation processes are generally controlled by soil moisture, temperature and substrate availability (Hutchinson *et al.*, 1997), they are extremely heterogeneous with space and time (Delmas *et al.*, 1997).

The total NH_3 volatilization was highly positively correlated with the total NO_x emission during the 22-day study period, although the N_2O fluxes were not. This means that the NH_3 and NO_x emissions are interactively favoured by similar soil and environmental conditions and that denitrification-induced N_2O emission probably narrowed any relation between it and the former gaseous N forms. This inference also accords with the highly significant relation for the total NH_3 and NO_x emissions with the total NH_4^+-N present in the upper soil layer. In contrast, experiment 1 showed rapid nitrification especially with the smaller urea granules, signifying the presence of NH_4^+-N was also the most responsive factor. Our results indicate that the point-placed USG could enhance NO_x emission by delaying nitrification, but that the rates of emission were remarkably lower compared to those obtained from surface-mixed or broadcasted urea.

4.4. Total gaseous N loss

It is clear that the combined value of the three gases (N_2O, NH_3 and NO_x) has an important impact on our assessment of the influence of urea granules on total gaseous N loss (except N_2). Considering both experiments, the USG-CL emitted four times more N than the -SiL, even regardless of the granule sizes used and 10% greater than the PU-treated silt loam soil. This means that point-placed USG could reduce gaseous N losses considerably, but with the exact effect being soil-specific. Results suggest that fine-textured soils treated with a single large urea granule could exacerbate N_2O emission, presumably because of the larger contribution of denitrification from anaerobic microsites, whereas medium-textured soils treated with PU, either mixed after broadcasting or broadcasted, could greatly influence NH_3 and NO_x emissions under aerobic conditions.

5. Conclusions

Coarse to medium textured soils (including PU-treated silt loam soil) released less N$_2$O as compared to a clay loam soil treated with a single large urea granule. By contrast, PU mixed at a shallower depth could induce greater losses of NH$_3$ followed by NO$_x$ over the use of a single large granule. From the management point of view, either surface mixing (if not thorough) or broadcasting of PU could emit a large amount of gaseous N. The high concentration gradients of NH$_4^+$, NO$_2^-$ and pH presumably delayed urease activity and nitrification, increasing N$_2$O emissions during nitrifier/chemo-denitrification. However, N$_2$O emission was in the lower reaches (up to 0.59%) of the generally accepted emission factor (1.25% of the added N). An exception to this trend could arise in the fine-textured soil, inducing more denitrified N$_2$O losses through the anaerobic microsites. We hypothesize that the point-placed larger urea granules might further reduce N$_2$O emission during crop growth period through the uptake of the mineral N that would be slowly becoming available through molecular diffusion or mass flow upon irrigation or rainfall events. As such, delaying nitrification and N$_2$O emission would therefore become advantageous. However, convective flow of the concentrated mineral N below the rooting zone resulting from intensive, but large irrigation or rainfall events during initial periods of dry/upland cropping may result in poor nitrogen use efficiency.

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