

soil layer respectively for N rates of 80, 160 and 240 kg ha<sup>-1</sup> of applied N. The maximum N accumulation zone was between 140 and 180 cm, independent of the amount of the N applied. Nitrogen leaching was observed without N fertilization if the growing season was dry and low N-demanding crops were grown.

The shifting of the water table after an extremely wet and dry period resulted in a huge NO<sub>3</sub>-N leaching from the accumulation zone.

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## UREA GRANULAR SIZES IN UPLAND SOILS: NITROGEN TRANSFORMATIONS AND MOVEMENTS INFLUENCING NH<sub>3</sub> AND NO<sub>x</sub> EMISSIONS

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#### Abstract

Information on the transformations and gaseous losses of N from upland agricultural soil urea super granules (USG) compared to prilled urea (PU) is meager. For technical decision supports, experiments were carried out with urea granular sizes (<2, 7.0, 9.9 and mm), soil type (sandy, silt and clay loams) and water regimes using PVC boxes controlled environmental conditions. High concentrations of NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup> and pH on longer with the large urea granule and at high but relatively constant soil water regime high concentrations were confined in less than 5 cm from the USG placement zone diffused slowly over time except irrigation events. These led to enhance N<sub>2</sub>O emissions nitrifier and/or chemo-denitrification were probably the dominant processes. Both nitrifi and N<sub>2</sub>O emissions were delayed for some days and half-values of total N<sub>2</sub>O fluxes appeared earlier with coarse than heavy textured soil. In 45 days, N<sub>2</sub>O emission potentials of PU smaller (≤0.17% of the added N) than of USG from all soils (0.25-2.61%), the highest with the clay loam. By contrast, NH<sub>3</sub> and NO<sub>x</sub> emissions were larger from PU (1.7-0.97% of the added N) than USG (0.27 and 0.29%, respectively) over 22 days, implying inhibition of urease activity. Both NH<sub>3</sub> and NO<sub>x</sub> emissions rose with the presence of mineral N/NH<sub>4</sub><sup>+</sup> in the surface layer. The NH<sub>3</sub> volatilization was proportional to the emission, indicating the regulatory factors to be alike. Pooled emissions reveal that the treated silt loam soil induced greater gaseous N losses (predominantly NH<sub>3</sub> and NO<sub>x</sub>) over large granules point-placed at 5 cm, and the USG-treated clay loam soil enhanced the noticeably where N<sub>2</sub>O took the major share. The N<sub>2</sub>O fluxes were best explained by NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and soil water contents, indicating the influence of both auto- and heterotrophic microbial activities.

## Introduction

Nitrous oxide (N<sub>2</sub>O), ammonia (NH<sub>3</sub>) and nitrogen oxides (NO<sub>x</sub>) 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. These gases have a major impact on the degradation of the atmosphere and various ecosystems. Anthropogenic activities have been responsible for the annual increases in N<sub>2</sub>O emissions over the past decade (Sowers, 2001), contributing to the greenhouse effect and ozone layer depletion. The formation of N<sub>2</sub>O 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 (Inubushi et al., 1996; Khalil et al., 2002a; Khalil and Baggs, 2005). In general, N<sub>2</sub>O 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 total N fertilizer applied.

Agriculture is the primary source of NH<sub>3</sub> and estimated to be 23% of global emission deriving from fertilizers and field-applied manure (Bouwman et al., 2002); even can range from ≈ 0 to >50% depending on fertilizer type, environmental conditions and soil properties (Sommer et al., 2004). NO<sub>x</sub> is also both directly and indirectly contributing to global warming, ozone depletion and acid deposition by controlling the tropospheric and stratospheric chemistry. NO<sub>x</sub> concentrations depend on the proximity of their sources because of their short atmospheric lifetime with anthropogenic sources represent only 30% of the total emissions (Delmas et al., 1997). The available information on the formation process of nitric oxide (NO) or NO<sub>x</sub> is conflicting, with during both nitrification and denitrification (Firestone and Davidson, 1989) or exclusively during nitrification (Russow et al., 2000) having been proposed. It is estimated that the increasing use of N fertilizers in agriculture will account for more than 50% of the global NO<sub>x</sub> budget by 2025 (Yienger and Levy II, 1995).

Globally, urea is the cheapest and mostly used commercial inorganic N fertilizer for agricultural production. 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<sub>2</sub>O (Mulvaney et al., 1997; Khalil et al., 2002b). Tenuta and Beauchamp (2000) showed that use of urea supergranule (USG) increased N<sub>2</sub>O production to a maximum of 1.24% of the added urea-N, with the presence of NO<sub>2</sub><sup>-</sup> being the dominant factor influencing its release. Besides, a high-localized urea/NH<sub>4</sub><sup>+</sup> concentration developed in the USG placement zone, followed by an increase in soil pH through enzyme-catalyzed 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 under aerobic conditions (Shah and Weber, 2003). Both broadcast and top-dressed prilled urea (PU) and deep-placed (4 cm) USG in light textured soils are prone to NH<sub>3</sub> volatilization (Buresh, 1987; Sommer et al., 2004). Mix urea with soils, a banded/deep placement, immediate rainfall/irrigation and rapid drying of surface soil after application might reduce these same losses (Bouwmeester et al., 1999; Weber et al., 2000; Khalil et al., 2005) depending on the soil type and water transmission. Further, high NH<sub>4</sub><sup>+</sup> concentrations could also facilitate NO<sub>x</sub> emissions under aerobic conditions (Russow et al., 2000).

It is clear that the USG, through their proper deep placement, are technologically and economically advantageous in lowland rice production (Savant et al., 1990; Mohanty et al., 1999). High amounts of NH<sub>3</sub> volatilization and N<sub>2</sub>O emission from soils treated with USG have been reported (Buresh, 1987; Tenuta and Beauchamp, 2000). However, uncertainty prevails on its use in upland crops with regard to agronomic efficiency, potential method application and with regard to the possible consequences of atmospheric and ground pollution. Thus, experiments were conducted to: (a) document the pattern and transport of mineral N from the zone of USG placement; (b) investigate the influence of urea granule soil water regimes and soil type on N<sub>2</sub>O, NH<sub>3</sub> and NO<sub>x</sub> emissions; and (c) elucidate interrelations between the gaseous N species over time and the factors affecting their emissions.

## Materials and Methods

### Soil characteristics

Field-moist soils were collected from three different locations of Southern Germany representing contrasting soil types, and passed through a 5-mm mesh sieve and stored in a dark cool (4-5 °C) place. The soils collected were silt loam (0-15 and 15-35 cm depths), sandy loam and clay loam, the latter two from 0-15 cm depth only. Some physical and chemical properties of these soils are presented in Table 1.

**Table 1:** Some physical and chemical properties of the experimental soils

Soils (USDA Taxonomy)	Land use	Particle size distribution (%)		pH	Org. C (%)	Total N (%)	C/N	CEC (cmol. kg <sup>-1</sup> soil)	
		Sand	Silt						Clay
1. Loamy-skeletal (Typic Udorthent)	Cereal-potato	60	29	11	5.2	1.25	0.14	9.3	10.8
2. Fine silty (Dystric Eutrochrept)	Legume grass (mixture)	20	60	20	6.4	1.61	0.17	9.5	17.6
3. Fine loamy (Dystric Eutrochrept)	Legume-cereal-potato	26	46	28	5.9	1.84	0.20	9.4	23.2

**Experiment 1: Soil water regimes**

Two separate experiments were conducted using polyvinyl boxes (1.10 m x 0.70 m x 0.40 m). Each box was filled with 5 cm of sand on the bottom followed by 20 cm of subsurface soil and the remaining 15 cm with the collected surface soil and watered to field capacity (70% water-filled pore space, WFPS at -33 kPa). This experiment consisted two urea granule size: prilled urea (PU, mixed into 7.5 cm depth) and urea supergranule (USG, point-placed at 7.5 cm depth) and two water regimes: around field capacity (AFC, soil water depletion at a slow rate from 77 to 69% WFPS) and below (BFC, with deliberate depletion in relatively high evaporative conditions from 69 to 55-56% WFPS, receiving two irrigations) through controlling temperature (17 and 20 °C) and humidity (85 and 55%, respectively). The urea for AFC and BFC was applied at a rate of 42.5 and 45.7 kg N ha<sup>-1</sup> and 15 USG (dia. ~8.6 and 8.8 mm; wt. ~0.427 and 0.459 g per USG, respectively) could be accommodated in a box. A gas chamber received either a USG or 0.086 and 0.093 g PU, respectively. Simulated irrigation water was added at 10 and 20 days after fertilization to BFC levels. Gas (six replicates) and soil (composite of four) were sampled up to 21 days for AFC and 30 days for BFC at days 0, 1, 2, 4, 7, 10, 11, 12, 15, 20, 21, 22, 25 and 30.

**Experiment 2: Urea granule size**

This experiment was designed to investigate the influence of various urea granule sizes at field capacity (70% WFPS). Urea fertilizer was applied to the pots (area of ~0.0127 m<sup>2</sup>) filled with the above but surface soil and thereafter watered to the desired level. Incubation was carried out at air temperature of 20 ± 2 °C. The treatments were N<sub>0</sub> - unfertilized control, PU - prilled urea (<2 mm), USGs- urea super granule small (dia. 7 mm; 0.25 g), USGm - USG medium (dia. 9.9 mm; 0.50 g) and USG1 - USG large (dia. 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. The Urea-N rate was 363 kg (181 mg N kg<sup>-1</sup> soil). Two separate experiments were conducted using 6 kg of dry soil i (0.20 m x 0.22 m in size) for N<sub>2</sub>O and CO<sub>2</sub> measurements and for NH<sub>3</sub> and NO<sub>x</sub> err. using PVC rings with a sealed bottom (0.13 m x 0.12 m) receiving 1.5 kg of dry soil. lost during the incubation period was replaced every three days and gas was sampled a 1, 3, 6, 9, 12, 16, 20, 25, 30, 37 and 45.

**Experiment 3: Soil type**

In this experiment, the air temperature was similar to that in experiment 2, but the em was on determining the effect of contrasting soil types with USG<sub>1,0</sub> point-placed at 5-c depth (sandy loam, USG-SL; silt loam, USG-SiL; and clay loam, USG-CL). An unfer control for each soil was also used. The soils were watered to field capacity [-10 kPa for loam (0.21 kg H<sub>2</sub>O kg<sup>-1</sup>) and -33 kPa for both silt loam (0.27 kg H<sub>2</sub>O kg<sup>-1</sup>) and clay (0 H<sub>2</sub>O kg<sup>-1</sup> oven-dry soil] and water lost during the incubation period was replaced every days. Otherwise, the experimental conditions were similar to experiment 2 except that rate was 366 kg N ha<sup>-1</sup> (182 mg N kg<sup>-1</sup> soil).

**Gas sampling and measurement**

For experiment 1, a closed chamber (volume 0.00167 m<sup>3</sup>) was used to collect gas. In th of USG treatment, the chambers were placed on the top of a USG placement zone (US well as on the unfertilized centre point of four USG placements (USG<sub>0,m</sub>). Twenty millilitr gas was collected using an airtight syringe from the headspace to analyze N<sub>2</sub>O an concentrations and the samples taken being analyzed using an automated gas chromat (Varian Star 3400, USA) equipped with electron capture and thermal conductivity det For experiment 2 and 3, gas was collected using a ventilated closed chamber (area 0.01 vol. 1.66 l) to measure N<sub>2</sub>O and CO<sub>2</sub> concentrations. To measure NH<sub>3</sub> and NO<sub>x</sub> emissio 22 days, PVC rings were filled with soil as per the treatments placed inside a d chamber (area 0.125 m<sup>2</sup>, dia 0.40 m, height 0.40 m). Each chamber was covered with glass that was fitted with a stainless steel ring and placed on a long tray filled with s measure gas fluxes over time. This method can measure both NH<sub>3</sub> and NO<sub>x</sub> simultaneo flowing the sample air to a two-channel chemiluminescence NO-Analyzer (CLD 700A EcoPhysics, Göttingen, CH).

**Soil analysis**

For experiment 1, soils were sampled up to a depth of 15 cm at 1.5, 5.0 and 8.5 cm di from the point of USG placement using a calibrated device. For experiment 2 and 3, soi sampled from 0 to 2.5 cm and 2.5 to 10 cm depths at the end of NH<sub>3</sub>/NO<sub>x</sub> study. A sub

was extracted with 1 M KCl at a soil: KCl solution ratio of 1:2.5 to determine  $\text{NH}_4^+\text{-N}$  colorimetrically with the salicylate method using a UV/VIS Spectrometer (Perkin Elmer, Lambda 20). Another subsample was extracted with 0.01 M  $\text{CaCl}_2$  at a soil:  $\text{CaCl}_2$  solution ratio of 1:2.5 to determine both  $\text{NO}_3^-$  and  $\text{NO}_2^-$  contents using HPLC (UVIKON 720LC, Shimadzu C-R3A Chromatopac). The latter extract was also used to measure soil pH using a glass electrode pH meter.

#### Statistical analysis

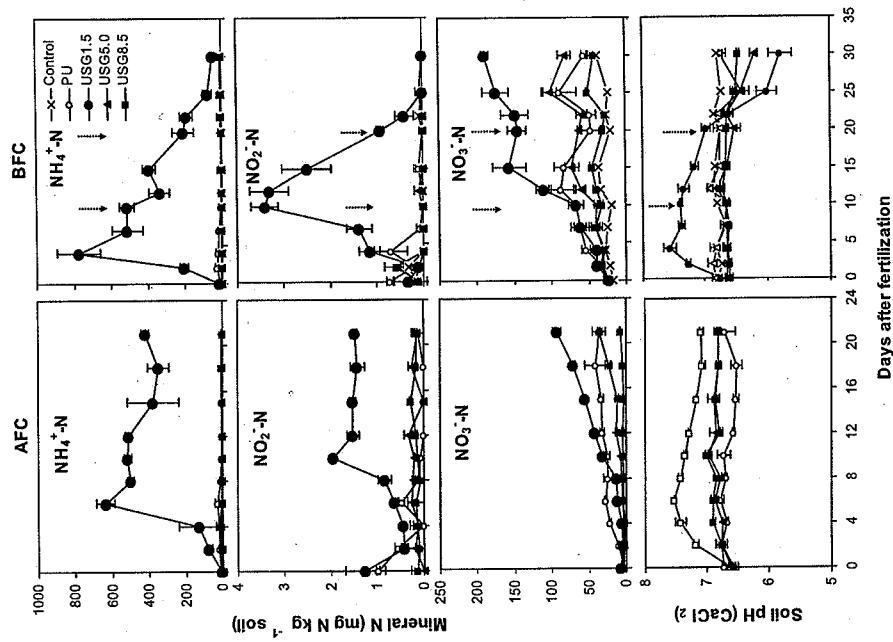
Statistical analyses were performed using the computer package JMP v4.0.2 of SAS Inc. An analysis of variance was computed at a probability level of 5% to test the significance of the treatment effects. Relative loss of the added N was calculated based on total  $\text{N}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{NO}_x$  fluxes under control or background emissions. Based on the rate of PU application, an average value for 1 USG<sub>in</sub> with 4 USG<sub>out</sub> was calculated (USG<sub>av</sub>) to provide an area that received the same amount of N to compare with the findings of the PU treatment. The day at which 50% of the total fluxes ( $t_{1/2}$ ) occurred was also identified. Simple and multiple regression analyses were performed to identify potential relationships between  $\text{N}_2\text{O}$  (as the independent variable) and various soil properties including  $\text{CO}_2$  (as dependent variables). For the USG treatment, the mineral N contents and pH of the two immediate distances (1.5 and 5.0 cm; USG<sub>in</sub>) and the remaining distance (8.5 cm; USG<sub>out</sub>) were considered for the corresponding  $\text{N}_2\text{O}$  fluxes for the regression analyses.

## Results and Discussion

### N transformations and movement

At both AFC and BFC, PU displayed an initial slow accumulation of  $\text{NH}_4^+$  before showing a relatively fast disappearance thereafter (Figure 1A, a). The concentration gradient of  $\text{NH}_4^+$  within the USG treatment was remarkably high next to the placement zone (USG<sub>1.5</sub>) and decreased slowly over time where the two irrigation events at BFC influenced the disappearance of  $\text{NH}_4^+\text{-N}$  over time strongly. The next soil sampling distance (USG<sub>5.0</sub>) demonstrated an increased  $\text{NH}_4^+$ , with its content remaining significantly higher than those for PU and USG<sub>8.5</sub> until the end of study.  $\text{NO}_2^-$  appeared short peaks at the beginning, immediately after the disappearance of  $\text{NH}_4^+\text{-N}$  (Figure 1B, b). Compared to PU, the concentration gradients of  $\text{NO}_2^-$  for the other two USG distances remained higher from day 10 onwards. Except for USG<sub>1.5</sub>, the  $\text{NO}_2^-$  concentrations were always lower at BFC than at AFC. The PU-treated soil showed an overall accumulation of  $\text{NO}_3^-$  with intermittent reductions (Figure 1C, c). The  $\text{NO}_3^-$  accumulation at USG<sub>1.5</sub> was slow initially and rose

linearly thereafter by 21 days. The concentration of  $\text{NO}_3^-$  also increased somewhat next sampling distances over time. Generally,  $\text{NO}_3^-$  accumulation was remarkably higher at BFC than at AFC.



**Figure 1:** Changes in mineral N content and pH over a 21- or 30-day period in a silt loam soil at two soil water conditions (AFC, BFC), below field capacity with rapid depletion (PU), and urea super granule at different soil sampling distances (USG<sub>1.5</sub>, USG<sub>5.0</sub>, USG<sub>8.5</sub>). Vertical bars indicate the days of irrigation to near field capacity and standard deviation respectively.

Results indicate that hydrolysis of urea was presumably delayed in the soil to which USG was applied, thereby resulting in high concentration gradients of  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and pH. The changes in soil pH over time for the two soil water conditions and different urea treatments support the trend of urea hydrolysis or ammonification and its oxidation (i.e. nitrification; Figure 1D, d). The findings are in agreement with other workers (Singh et al., 1994; Tenuta and Beauchamp, 2000); Shah and Wolfe (2003) also reported decreased dissolution with increasing urea size. The high concentration gradients, however, were limited up to <5.0 cm from the zone of a USG placement, indicating the likely molecular diffusion of  $\text{NH}_4^+$  after hydrolysis of USG followed by nitrification. However, the diffusion of  $\text{NH}_4^+$  was small at AFC presumably due to the limitation of exchange sites around the zone of USG placement (Shah and Wolfe, 2003). The involvement of mass flow, if any, might take place at the later time periods and when soil water content at the zone of USG placement remained high (Singh and Beauchamp, 1988). The lower recovery as  $\text{NO}_3^-$  in comparison to  $\text{NH}_4^+$  disappearance over time indicated an involvement of other N transformation mechanisms (Khalil and Baggs, 2005; Müller et al., 2004). Nitrification in this situation was either inhibited or slowed down.

### **N<sub>2</sub>O emissions**

N<sub>2</sub>O emissions varied greatly between the two different soil water regimes (Experiment 1), with peak or total emissions (Table 2) being higher at AFC than for that at BFC. As such, the two soil water conditions considerably influenced the relative N<sub>2</sub>O losses from the added N and it was higher with USG<sub>in</sub> at AFC (0.20%) than at BFC (0.10%) though receiving two irrigation events (Table 2). The increased emission at AFC was probably linked more either biological (Bremner, 1997; Wrage et al., 2001, 2004) and/or chemo-denitrification, (Van Cleemput, 1998), by creating anaerobic micro sites through enhanced soil respiration (Azam et al., 2002). This process was accelerated by the already relatively constant but high soil water content (Khalil and Baggs, 2005). The relative N<sub>2</sub>O lost over the entire 21-day period was several-fold greater from USG<sub>in</sub> (0.10-0.20%) point-placed than for the PU mixed into (0.04-0.06%) 7.5 cm depth. Similar losses with small urea granules (Hosen et al., 2002) and higher losses with large granules (Tenuta and Beauchamp, 2000) have also been reported. The response differences may be correlated with the different management, experimental and environmental conditions of the studies (Khalil et al., 2002a, b). There was, however, a small difference between the PU and USG<sub>in</sub> treatments at BFC.

During the 45 days of the incubation, the total N<sub>2</sub>O fluxes were enhanced with increasing granule size although the two immediate sizes responded identically and it was 6-8 times

higher in the clay loam over the other two soils, with the value in the sandy loam being higher than that for the silt loam (Table 2). The relative loss of urea-N as N<sub>2</sub>O was enhanced with increasing urea granule size (experiment 2), ranging from 0.17-0.50% of the added over the 45-day period, when either PU was mixed into a silt loam soil or USG were placed into it at 5.0-cm depth. Similar and higher N<sub>2</sub>O emissions with a large USG (1.24%) applied in a silt loam soil have also been reported (Tenuta and Beauchamp, 2000). When a large USG (12.7 mm dia) was point-placed at 5.0 cm to the three contrasting (experiment 3), the N<sub>2</sub>O loss of the added N from the USG-SiL was similar to that of experiment 2 (0.53%), although the maximum peaks were attained somewhat earlier (Table 2). The USG-SL released a slightly higher amount of N<sub>2</sub>O (0.59%), whereas the control (Table 2) released several-fold larger N<sub>2</sub>O emissions than the USG-SiL, indicating the influence of low values towards increasing the mole fraction of N<sub>2</sub>O during nitrification in the form (Mullvaney et al., 1997; van Cleemput, 1998; Khalil et al., 2002b). The N<sub>2</sub>O loss of the added N was several-fold greater in the USG-CL (2.61%) than the other two soils. This remaining N loss from the clay loam soil might be attributable to the major contribution of denitrification process, relating to high water-filled pore space (Khalil and Baggs, 2005). Besides, N<sub>2</sub>O emission increased with increasing sizes of USG (Tenuta and Beauchamp, 2000) and loads of N fertilizer (Khalil et al., 2004), where high-localized NO<sub>2</sub><sup>-</sup> concentrations are important factors. The differences among the soils also imply that soils having large pore spaces might also enhance N<sub>2</sub>O emission because soil N is generally held in the major source.

For experiment 1, 50% of total N<sub>2</sub>O production (t<sub>1/2</sub>) was achieved 2-5 days earlier for the PU than AFC over the 21-day period, whereas it was delayed by 4-6 days in the USG treatment compared to the PU treatment (Table 3). The t<sub>1/2</sub> was further extended by a few days although this experiment experienced two irrigation events. For experiment 2 over the 21-day period, the t<sub>1/2</sub> occurred was delayed between 1 and 9 days with larger granule size although two immediate sizes responded identically. In the case of experiment 3, it was delayed 2-4 days over the respective control treatments, and more so for the USG-CL (Table 3). The point at which t<sub>1/2</sub> of the total emissions were achieved confirmed that N<sub>2</sub>O emission from the PU was delayed for several days over PU, in line with other workers (Tenuta and Beauchamp, 2000; Khalil et al., 2005). We found that the delay in reaching 50% emission varied with granule size and soil type, with the day of occurrence of the larger peaks appearing during the study periods.

**Table 2:** Total (g N ha<sup>-1</sup>) and relative N<sub>2</sub>O loss of added N (%) during 21 or 45 days at two soil water regimes, urea granule size and soil type

Treatment	Control	PU	USG <sub>in</sub> /USGs	USG <sub>out</sub> /USG	USG <sub>w</sub> /USGI
AFC (77-69% WFPS)		0.06 (146.0)	0.20 (208.3)	0.11 (169.6)	0.13 (177.3)
BFC (69-56% WFPS)		0.04 (99.3)	0.10 (127.9)	0.04 (101.5)	0.05 (106.8)
Urea granule size (70% WFPS)		0.17 (675.9)	0.25 (992.1)	0.44 (1671.3)	0.50 (1916.7)
Soil type (70% WFPS)					
Sandy loam	(665.9)				0.59 (2791.1)
Silt loam	(87.0)				0.53 (2017.5)
Clay loam	(1732.8)				2.61 (11218.6)

AFC, around field capacity; BFC, below field capacity; PU, prilled urea; USG<sub>in</sub> and USG<sub>out</sub>, urea super granule (placement of chamber on the top of a USG and on unfertilized space between four USGs, respectively); USG<sub>w</sub>, average values of USG<sub>in</sub> (1) and USG<sub>out</sub> (4); USGs (small, 0.25 g); USGm (medium, 0.50 g); USGI (large, 0.10 g). Figure in parenthesis is total N<sub>2</sub>O flux

**Table 3:** Day at which half of total N<sub>2</sub>O-N was lost (t<sub>1/2</sub>), during 21 or 45 days at two soil water regimes and urea granular sizes

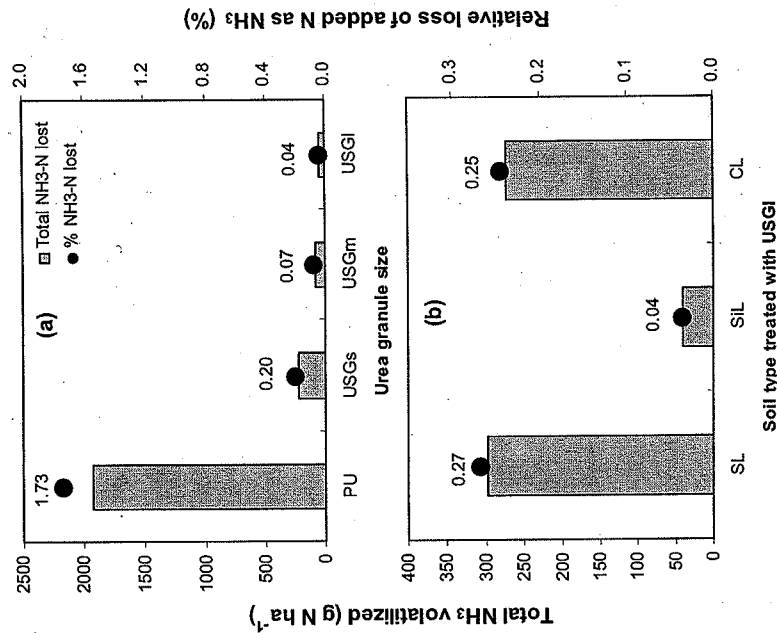
Treatment	PU	USG <sub>in</sub> /USGs	USG <sub>out</sub> /USGm	USG <sub>w</sub> /USGI
AFC (77-69% WFPS)	5	8	7	-
BFC (69-56% WFPS)	12	18	14	-
Urea granule size (70% WFPS)	18	17	23	26

AFC, around field capacity; BFC, below field capacity; PU, prilled urea; USG<sub>in</sub> and USG<sub>out</sub>, urea super granule (placement of chamber on the top of a USG and on unfertilized space between four USGs, respectively); USG<sub>w</sub>, average values of USG<sub>in</sub> (1) and USG<sub>out</sub> (4); USGs (small, 0.25 g); USGm (medium, 0.50 g); USGI (large, 0.10 g)

### NH<sub>3</sub> volatilization

The total NH<sub>3</sub> loss over the 22 days was noticeably the highest for the PU treatment and then for those treatments with the larger granules, showing the greatest from the sandy loam, followed by the clay and silt loam soils (Figure 2). In contrast to the pattern observed for N<sub>2</sub>O emissions, NH<sub>3</sub> volatilization decreased with increasing granule size, with the PU-treated silt loam soil emitting several-fold higher level (1.73% of the added N) than did the same soil treated with the larger urea granules (0.04-0.20%; Figure 2a). This could largely be explained by NH<sub>3</sub> volatilization being a surface-related process. As such, the loss of NH<sub>3</sub> would increase

with the application of urea and ammonium-based fertilizers to the soil surface (Bouwn et al., 1985), a movement of urea- and/or ammoniacal-N to the soil surface during the process (Ferguson and Kissel, 1986) and a prolonged formation of ammoniacal-N in (Buresh, 1987). The NH<sub>3</sub> volatilization was also small from the three contrasting soil USG point-placed at 5.0-cm depth, ranging from 0.04-0.27% of the added N, with the value being obtained from the silt loam soil (Figure 2b).



**Figure 2:** Total NH<sub>3</sub> volatilized and its relative loss of the added N over a 22-day period in a silt loam soil with urea granule size (a) and soil type treated with USGI (b) at field [PU, prilled urea; USG, urea super granule; USGs (small, 7.0 mm); USGm (medium, 7.0 mm); USGI (large, 12.7 mm)]

The share of mineral N in the 0-2.5 cm soil surface layer was by far the highest (90% PU-treated soil (Figure 3a), also supports the above findings. However, the percent

mineral N in the 0-2.5 cm surface layer among the three soils had an inconsistent influence on NH<sub>3</sub> losses (Figure 3b).

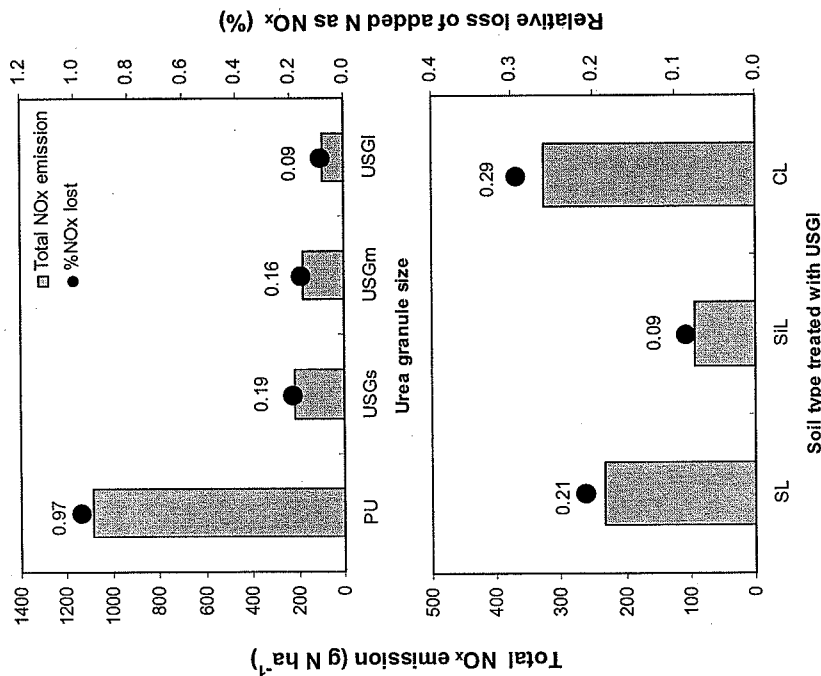


Figure 3: Total NO<sub>x</sub> emission and its relative loss of the added N over a 22-day period from a silt loam soil with urea granule size (a) and soil type treated with USGI (b) at field capacity [(PU, prilled urea; USG, urea super granule; USGs (small, 7.0 mm); USGm (medium, 9.9 mm); USGI (large, 12.7 mm)]

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 exchange sites coupled with the anaerobic situation presumably acted as a barrier for NH<sub>3</sub> 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 2005) and the limitation of urease activity imposed by high urea concentrations (Son et al., 2004) might be advantageous in reducing NH<sub>3</sub> volatilization. In contrast to our findings, small NH<sub>3</sub> volatilization even from the sandy loam soil, Buresh (1987) reported a large loss (up to 67%, with variation in some soils of 2.9- 4.1%) from 1.1 g of USG (point-p) 4 cm into several coarse textured soils. Possible reasons for the different findings include the shallower placement, larger sand content, and lower H<sup>+</sup> buffering capacity (carbon content in the soils examined by Buresh. Our results indicate that mixing PU soil at a depth of 5 cm or more could greatly reduce NH<sub>3</sub> volatilization compared to mixing/broadcasting method, as has also been reported by others (Weber et al., 2001; Wang et al., 2004; Wang et al., 2004; Khalil et al., 2005). Point-placed large USG could decrease NH<sub>3</sub> volatilization but the effect is soil-specific, in agreement with the results of (1989) who found that 1.47-3.07% was lost from an upland system. Soils having buffering capacities might prevail over the high concentration gradients of NH<sub>4</sub><sup>+</sup> which occur in the placement zone only (Khalil et al., 2005), leading to the exchange of NH<sub>3</sub> vapor with the upper soil portions. However, this result is presumably to receiving either controlled irrigation (preferably after fertilization) or small rainfall (Bouwmeester et al., 1985).

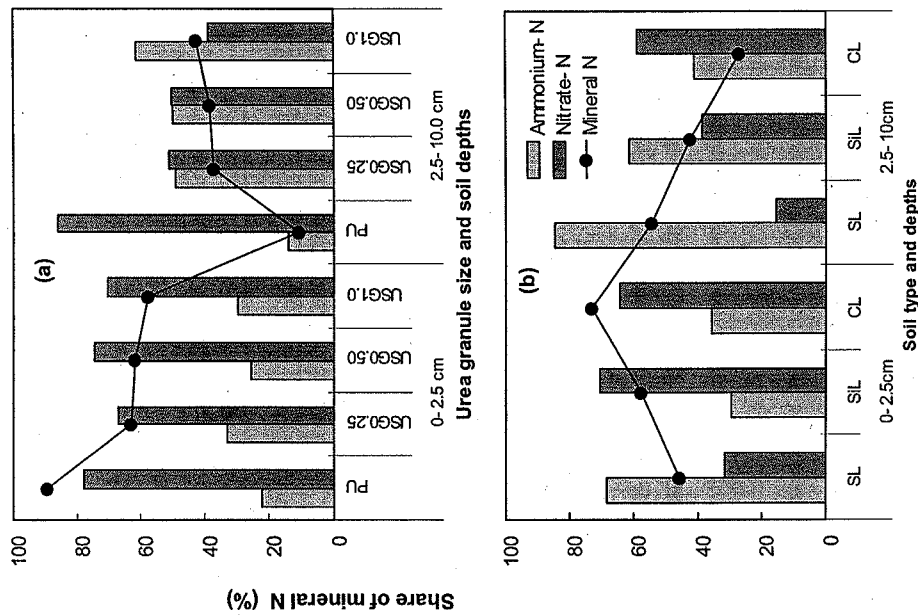
#### NO<sub>x</sub> emissions

The total NO<sub>x</sub> flux was highest for the PU treatment and in contrast to NH<sub>3</sub> volatilization emission increased with decreasing urea granule size, showing higher for the clay loam sandy loam soils treated with the largest granule (Figure 4). As such, the PU mixed soil released several-fold greater levels of NO<sub>x</sub> (0.97% of the added N) compared to the granule sizes (0.09-0.19%; Figure 4a). Hou and Tsuruta (2003) found similar percent NO-N loss when broadcasted urea was mixed to a 15-cm depth by ploughing down (or band-placed at a 12-cm depth (-0.03%, calculated). However, NO<sub>x</sub> emissions were than that reported with broadcast urea (1.5%) by Weber et al. (2001). Similarly, its emission was also small from the USG-SL and USG-CL (0.21-0.29%), but considerably higher from the USG-SIL (Figure 4b). This indicates that NO<sub>x</sub> emission is soil-specific (probably limited by the presence of solution and gas phase in the respective soils (Skl 1997) or that soil consumption was occurring (Hou and Tsuruta, 2003). The positional differences in mineral N concentrations, as was the case for NH<sub>3</sub> to support the trends for NO<sub>x</sub> emission. During the N<sub>2</sub>O measurements, it was found

nitrification was delayed with increasing urea granule size but remained the dominant process. This implies that nitrification was primarily responsible for  $\text{NO}_x$  production and release under aerobic conditions, in agreement with the findings of other researchers (Russow et al., 2000; Zheng et al., 2003). The presence of comparatively more  $\text{NH}_4^+$  in the surface compared to sub-surface layers for subsequent nitrification could possibly influence  $\text{NO}_x$  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  $\text{NO}_2^-$  as an electron acceptor during  $\text{O}_2$  limiting conditions (Remde and Conrad, 1990). It should be pointed out, however, that  $\text{NO}_x$  is typically not a major end product of N transformations in anaerobic soil systems (Davidson, 1993) or serves as sinks (Remde et al., 1989). Furthermore, although the  $\text{NO}_x$  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).

#### Total gaseous N loss

For experiment 2, the relative gaseous N loss ( $\text{N}_2\text{O} + \text{NH}_3 + \text{NO}_x$ ) of the added N was several fold higher for the PU treatment (2.87%) than for the larger granules (0.63-0.67%). In the case of soil type treated with a large granule, combined gaseous N loss was several-fold higher from the clay loam (3.15%) than for the sand loam (1.07%) and silt loam (0.66%). Results show an important impact on our assessment of the influence of urea granules on total gaseous N loss (except  $\text{N}_2$ ). The PU-treated silt loam soil demonstrated gaseous N losses that were about four times higher than that from any of the larger granules, which were almost identical (0.63-0.67% of the applied N). Similarly, the USG-CL emitted four times more N than the USG-SIL regardless of the granule sizes used and 10% greater than the PU-treated silt loam soil. Again, 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 USG could exacerbate  $\text{N}_2\text{O}$  emission, presumably because of the larger contribution of denitrification from anaerobic micro sites, whereas medium-textured soils treated with PU, either broadcast or mixed after broadcasting, could greatly influence  $\text{NH}_3$  and  $\text{NO}_x$  emissions under aerobic conditions.

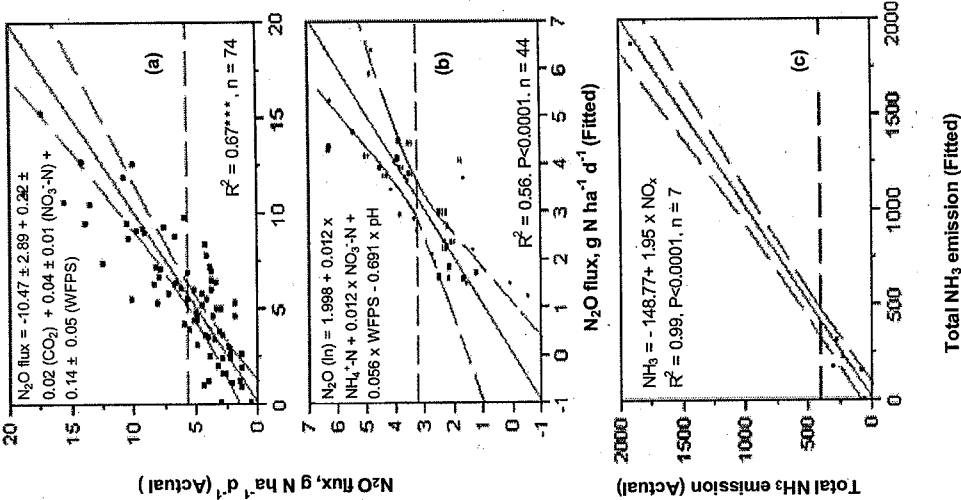


**Figure 4:** Concentration of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  N both individually and combined at the end of  $\text{NH}_3$  and  $\text{NO}_x$  study (22 days) in the surface and sub-surface layers as influenced by urea granule size (a) and soil type treated with USGI (PU = prilled urea; USGx = urea su granule of weight x in grams (corresponding dia. 7.0, 9.9 and 12.7 mm; SL = sandy loam; SIL = silt loam; CL = clay loam)

#### Relationships

Gaseous N losses were related primarily to changes in soil properties. Combining the analysis from the two soil water regimes (AFC and BFC), it was found that the  $\text{N}_2\text{O}$  fluxes could





**Figure 5:** Actual and fitted (predicted)  $N_2O$  fluxes ( $g N ha^{-1} d^{-1}$ ) irrespective of soil regimes (a) and urea granule size and soil type (b), along with the corresponding soil influencing its emission as well as correlation between total  $NH_3$  and  $NO_x$  emission their regression equations with the coefficients of determination ( $CO_2 = kg C ha^{-1} day^{-1}$  &  $NO_3-N = mg N kg^{-1} soil$ ; water-filled pore space, WFPS = %, Total  $NH_3$  at emission ( $g N ha^{-1}$ ))

described best by  $CO_2$ ,  $NO_3^-$ ,  $NO_2^-$ , and WFPS (Figure 5a). A similar but strong relationship for  $N_2O$  with mineral N and  $CO_2$  (Tenuta and Beauchamp, 2000) as well as between  $N_2O$  and mineral N together with WFPS under field conditions (Khalil et al., 2002a) have also been reported. In addition, the increase in  $N_2O$  emissions or its pattern of release might change with the available oxidisable C i.e. soil respiration (Azam et al., 2002) and soil water regimes (Hosen et al., 2002). Thus, the activities of both auto- and heterotrophic microbes could be equally important to  $N_2O$  emission and that soil water is also an important factor for controlling the processes (Khalil et al., 2005); the latter observation is notably in agreement with those of others (Hosen et al., 2002; Tenuta and Beauchamp, 2003). Considering urea granule size and soil type, the relationship between  $N_2O$  and soil variables indicate that the formation and release of  $N_2O$  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 (Figure 5b). However, soil pH might be dominant over the influence of  $CO_2$  on  $N_2O$  emissions when contrasting soils were taken, and the impact of acidic soils for enhancing  $N_2O$  emissions has also been reported (Mulvaney et al., 1997; Van Cleemput, 1998; Khalil et al., 2002b). 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. Results suggest that soil water content can be an important regulatory factor towards autotrophic and heterotrophic microbial activities and thus,  $N_2O$  emissions. Point-placed USG could increase gaseous N losses somewhat, but also delay nitrification and  $N_2O$  release, depending on the soil water content and the existence of a high  $NO_2^-$  concentration.

The total  $NH_3$  volatilization was highly positively correlated with the total  $NO_x$  emission during the 22-day study period (Figure 5c), although the  $N_2O$  fluxes were not. This means that the  $NH_3$  and  $NO_x$  emissions are interactively favored 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. But it is in contrast to experiment 2, where the presence of  $NH_4^+-N$  and subsequent nitrification, especially with the smaller urea granules, were the most responsive factors. Our results indicate that the point-placed USG could enhance  $NO_x$  emission by delaying nitrification, but that the rates were remarkably lower compared to those obtained from surface-mixed or broadcast urea.

### Conclusions

The high concentration gradients of  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and pH in the placement zone of USG were limited to a distance of <5 cm under aerobic conditions. The presence of high  $\text{NO}_2^-$  concentrations over time and probable (true/nitrifier or chemo) denitrification from anaerobic micro sites enhanced  $\text{N}_2\text{O}$  emissions around field capacity. Indeed, the  $\text{N}_2\text{O}$ -N loss from the added N over the 21-day period in either urea size is small ( $\leq 0.20\%$ ).  $\text{N}_2\text{O}$  release increased with the increase in urea granular size, which is more conducive to a clay loam soil than to coarse to medium textured soils (as compared to PU-treated silt loam soil). From the management point of view, either surface mixing (if not thorough) or broadcasting of PU could emit a large amount of gaseous N. However,  $\text{N}_2\text{O}$  emission was in the lower reaches (up to 0.59%) of the generally accepted emission levels (1.25% of the added N). We hypothesize that the point-placed larger urea granules might further reduce  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  emission would therefore become advantageous particularly at soil water content below field capacity. By contrast, PU mixed at a shallower depth could induce greater losses of  $\text{NH}_3$  followed by  $\text{NO}_x$  over the use of a single large granule. Results suggest that  $\text{N}_2\text{O}$  emissions might result from both auto- and heterotrophic microbial activities, and that soil water regulated the processes greatly. The mixing of PU into the soil could reduce  $\text{N}_2\text{O}$  emissions to some extent compared to point-placed USG, but with the effects being soil specific (with USG-CL showing the most favorable results), contrasting for  $\text{NH}_3$  and  $\text{NO}_x$  emissions and thus, point-placed USG could reduce overall gaseous N losses considerably.

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