

Loss of nitrogen by ammonia volatilisation and denitrification after application of urea to maize in Shanxi Province, China

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Abstract. Much of the fertiliser nitrogen (N) used in agriculture is lost to the atmosphere as nitric oxide and nitrogen dioxide (collectively referred to as NO_x), ammonia (NH₃), and nitrous oxide (N₂O). The lost N is not only an economic problem for the farmer; it also contaminates the environment and affects human health. Because the values obtained for NO_x and NH₃ loss to the atmosphere from agriculture in Monsoon Asia have been questioned, we quantitatively determined, using new techniques, the emission of these gases from a maize crop fertilised with urea in northern China. The fertiliser was deep-placed by traditional farmers' practice and emissions of NO_x and NH₃ were determined with a chemiluminescence analyser and a backward Lagrangian stochastic dispersion technique. The emission measurements indicate that 1.2% of the applied N was lost as NO_x. This loss is far greater than measured or derived by other researchers, and we suggest that this is because our measurements were made continuously rather than as spot measurements with static chambers. The results for NH₃ show that, although the fertiliser was placed below the soil surface, a small amount (7% of the applied N) was still lost to the atmosphere. Soil analyses indicate that the rate of nitrification in this soil was low, and the maximum nitrate (NO₃⁻) concentration found in the soil (31.4 µg N/g) was only 3.9% of the fertiliser N added. Thus, there is little potential for NO₃⁻ to be leached down the profile. A study using soil cores and acetylene inhibition to measure denitrifying activity suggested that the rate of denitrification in this soil was also very low. The results suggest that in this soil with slow nitrification and denitrification rates and little potential for leaching, deep placement of the urea to limit NH₃ volatilisation is an effective method for increasing fertiliser use efficiency.

Additional keywords: bLs method, deep placement, fertiliser, micrometeorological techniques.

Introduction

Agriculture in China is highly intensive and, with the aid of new technology and high input of fertiliser, is very productive and meets the demands by the rapidly increasing population for food and animal feed (Zhu and Chen 2002). Maize is the second most important cereal crop in China (FAO 2009), and as a feedstuff has played an important role in the rapid development of poultry and livestock industries (Meng *et al.* 2006). Most of the maize produced in China is grown in the northern part of the country in the provinces Heilongjiang, Jilin, Liaoning, Hebei, Henan, Shanxi, Xinjiang, Zhenyuan, and Gansu (~70% of the total area planted) where yields in the last 50 years have increased from 1180 to 5000 kg/ha, mainly as a result of the application of fertiliser nitrogen (N) (Zhen *et al.* 2006; Goa *et al.* 2009).

Due to lack of direction, many farmers have applied too much fertiliser N, which has resulted in low N use efficiency (Goa *et al.* 2009). The reason for the low efficiency is that much of the applied N is lost from the plant–soil system as ammonia (NH₃), nitric oxide and nitrogen dioxide (NO and NO₂, collectively

NO_x), nitrous oxide (N₂O), dinitrogen, and nitrate (NO₃⁻) by volatilisation, denitrification, erosion, runoff, and leaching (Zhu and Chen 2002; Yan *et al.* 2003).

The lost N is not only an economic problem for the farmer; it can also affect human health and contaminate the environment (Galloway *et al.* 2008). The NO_x produced during nitrification and denitrification leads to the formation of tropospheric ozone, which induces respiratory tract inflammation and leads to short-term reductions in lung function in humans (Townsend *et al.* 2003). When NO_x and NH₃ react together they can form fine, particulate, secondary aerosols (PM_{2.5}), which can cause cardiovascular and respiratory diseases, and overall mortality (Townsend *et al.* 2003). In addition, the secondary aerosols play important roles in climate forcing by affecting the radiative balance in the Earth's atmosphere and influencing cloud formation (IPCC 2007).

The values obtained for NO_x and NH₃ emission from agriculture in Monsoon Asia have been questioned (Wang *et al.* 2004; McElroy and Wang 2005; Yan *et al.* 2005). One

reason for the uncertainty of the NO_x values is that most have been obtained as spot measurements with chambers (Veldkamp and Keller 1997). Veldkamp and Keller (1997) found sharp peaks of emissions during the first few days after fertilisation, and that the chance of missing a peak is relatively high if measurements are made only at weekly or monthly intervals. They concluded that infrequent measurements probably result in underestimates for total NO emissions.

Consequently, an experiment using micrometeorological techniques was conducted in Shanxi Province, northern China, on a maize crop fertilised with urea to provide continuous measurements of NO_x emission and NH_3 volatilisation and to determine the importance of the different loss processes in that environment.

Material and methods

The experiment was conducted at the Shanxi Academy of Agricultural Sciences research station, Yongi ($34^\circ 56' \text{N}$, $110^\circ 43' \text{E}$), Shanxi Province, China, in July 2008. The cultivated horizon (0–0.20 m) of the soil at the site contained 16.6% sand, 46% silt, and 37.4% clay. It had an initial pH (1 soil:5 water) of 8.5 and contained 9.6 g/kg of organic C, 1.09 g/kg of total N, 6.3 μg N/g soil as ammonium (NH_4^+), and 5.1 μg N/g soil as NO_3^- . The bulk density of the soil was 1.23 g/cm³.

Maize (variety Nongda 108) was seeded on 6 June, after harvesting wheat, into a rectangular field 200 m by 100 m. On the day that urea was applied there were ~44 000 maize plants/ha. On average, the rows were 62.1 cm apart and the plants in each row were 36.7 cm apart. A rectangular plot with sides of 64 and 52 m in the middle of the planted area was fertilised with urea; a weighed amount of prilled urea (60 kg N/ha) was applied at a depth of ~50–100 mm by the traditional point deep-placement technique (used by Zhang *et al.* 1992; Cai *et al.* 2002b) on 9 July (33 days after seeding) at 0900–1100 hours, and 1600–1830 hours. The application, by a group of farmers, involved removal of a small amount of soil adjacent to a maize plant with a hoe, addition of a calculated amount of urea to the hole by hand, and covering the urea with soil. In order to find the locations of the fertilised areas for subsequent soil analysis, a large number of fertilised areas were randomly selected and the centres were marked with wooden pegs. Emission measurements commenced the next morning, i.e. one day after fertilisation (34 days after seeding), when the maize was 65 cm high. The maize grew at the rate of 3.8 cm/day.

Emission measurements

Ammonia volatilisation was determined through application of a micrometeorological backward Lagrangian stochastic (bLs) dispersion technique (Flesch and Wilson 2005) that infers rates of emissions of gases from defined source areas using measurements of gas concentrations upwind and downwind of the area. The bLs technique uses a Lagrangian dispersion model to simulate the trajectories of air parcels arriving at the gas sensors and traces the parcels backwards from the sensors. The numbers of 'touchdowns' (intersection of these trajectories with the surface) of parcels in the source area and outside it provide the means to attribute the gas flux to emissions from the source

and background areas. The bLs model requires only a single measurement of concentration downwind of the source, with flexibility in the measurement location, if the background concentration is known (Flesch *et al.* 2005). The simulated ratio of the atmospheric gas concentration measured by the sensor C_g to the rate of emission from the source area F_0 is given by:

$$(C_g/F_0)_{sim} = (1/n)\Sigma|2/w_0| \quad (1)$$

where n is the number of simulated trajectories (50 000 in the present application) and w_0 is the vertical velocity of particles at touchdown. Then the actual emission rate is given by:

$$F_0 = (C_g - C_b)/(C_g/F_0)_{sim} \quad (2)$$

where C_b is the background (upwind) concentration. The calculations that are required to evaluate Eqns 1 and 2, as well as the specification of source and background areas and the type and location of sensors, are facilitated by use of the software package WindTrax (WindTrax 2006). The simulations require measured statistics of the atmospheric turbulence as well as the height and locations of the sensors, and the wind speed and direction. Turbulence statistics and wind speed and direction were measured with a 3-D sonic anemometer (Campbell Scientific CSAT-3) installed within the large maize field just outside the fertilised area, ~30 m from the gas-sampling point. Ammonia and NO_x concentrations were measured with a chemiluminescence analyser (Model EC9842Trace; Ecotech, Melbourne, Vic.) installed near the centre of the fertilised plot, and sample lines (6-mm-diameter polyethylene tubing) were run to the analyser from intake points at the centre of the fertilised area, and 10 m upwind of the plot boundary to measure background concentrations. Measurements of NO_x and NH_3 concentrations were made initially at 1.5 m above the ground, increasing to 2 m as the crop grew. The analyser measures NO concentrations in the air stream directly, and NH_3 and NO_2 concentrations after the stream has passed through converters to change them to NO. Briefly, the analyser specifications are: range 0–2 ppm NH_3 , resolution 0.1 ppb, precision $\pm 1\%$ of reading, and sample flow rate 900 cc/min (Dal Sasso 2010). We obtained 1-min averages of gas concentrations.

Denitrification

The study area was divided into three blocks representing the western, central, and eastern sections, and field-moist soil samples were collected from this area on 7 July, before the application of fertiliser, and at intervals after fertiliser application, using a soil corer with an external diameter 4.46 cm. In each block, five replicate cores at depths of 0–0.15, 0.15–0.30, 0.30–0.45, 0.45–0.60, and 0.60–0.75 m were taken from the centre of the marked fertilised areas, and the individual layers were combined for the denitrification assay and analysis of urea and mineral N (3 blocks \times 5 depths = 15 samples for analysis).

The denitrification rates at the five different depths were determined by an acetylene inhibition method (Aulakh *et al.* 1991) every second day at the beginning of the study and every third day at the end. The method involved placing the cored

samples in a 472-mL plastic jar sealed with a screwed lid fitted with a rubber septum for gas sampling. Acetylene (100 mL/L) was added via the rubber septum and the samples were incubated at field temperature for 6 h. The jar headspace was sampled for N₂O at 0, 2, and 6 h by removing a 13-mL gas sample with a syringe and transferring it to a 12-mL vacutainer. These samples were analysed for N₂O using a gas chromatograph fitted with a Ni⁶⁵ electron-capture detector and for carbon dioxide (CO₂) on a chromatograph fitted with a flame ionisation detector. The denitrification flux (*F*) was calculated from the formula:

$$F = (V/A)(\Delta c/\Delta t) \quad (3)$$

where *V* is the volume of the headspace, *A* is the area of the base, and $\Delta c/\Delta t$ is the change in gas concentration with time. The rate of CO₂ production (respiration) was determined by the same formula.

Soil analysis

On each occasion, 10 g of moist soil from the different depths was taken and placed in a 50-mL wide-mouth plastic bottle, and 20 mL of 2 M KCl containing 5 mg/L phenylmercuric acetate solution was added. The soil suspensions were shaken for 1 h then filtered through a Whatman No. 42 filter paper. The filtrate was collected and kept in a freezer (−20°C) until analysed for urea, NH₄⁺, and NO₃[−]. Nitrate was determined in samples from the five depths, but urea and NH₄⁺ were determined in the 0–0.15 m layer only. In the soil extracts, urea was determined using a modified diacetymonoxime method (Mulvaney and Bremner 1979), and NH₄⁺ and NO₃[−] were determined by a colourimetric procedure using a Technicon Autoanalyser (Rayment and Higginson 1992).

As the fertiliser was applied close to the soil surface, a second set of soil samples was taken from the 0–0.05 m soil layer to follow the trends in urea hydrolysis and nitrification. Five soil samples were taken from the marked fertilised areas in each of the three blocks. In order to limit analytical work, the 15 samples were combined into one for analysis of urea, NH₄⁺, and NO₃[−].

Soil water-filled pore space (WFPS) was calculated using the formula:

$$\text{WFPS} = \theta / \left(1 - \frac{\text{BD}}{\text{PD}} \right) \times 100\% \quad (4)$$

where θ is volumetric soil water content, BD is soil bulk density, and PD is particle density, assumed to be 2.65 g/cm³ (Aulakh *et al.* 2000).

Statistical analyses

All data were analysed using the MINITAB statistical package (Minitab 2010). Analysis of variance was used to assess the effects of time and depth of sampling on the measured variables.

Results and discussion

One day after fertilisation (1 DAF) the moisture content of the 0–0.05 m surface soil was 14.6% and this decreased to 9.1% at 4 DAF. The moisture content at 13 DAF had increased to 24.4% following three days of rain. The WFPS in the 0–0.05 m layer varied from 33.5% at 1 DAF to 56% at 13 DAF, but for a long period between these times the WFPS was <30% (Fig. 1). At

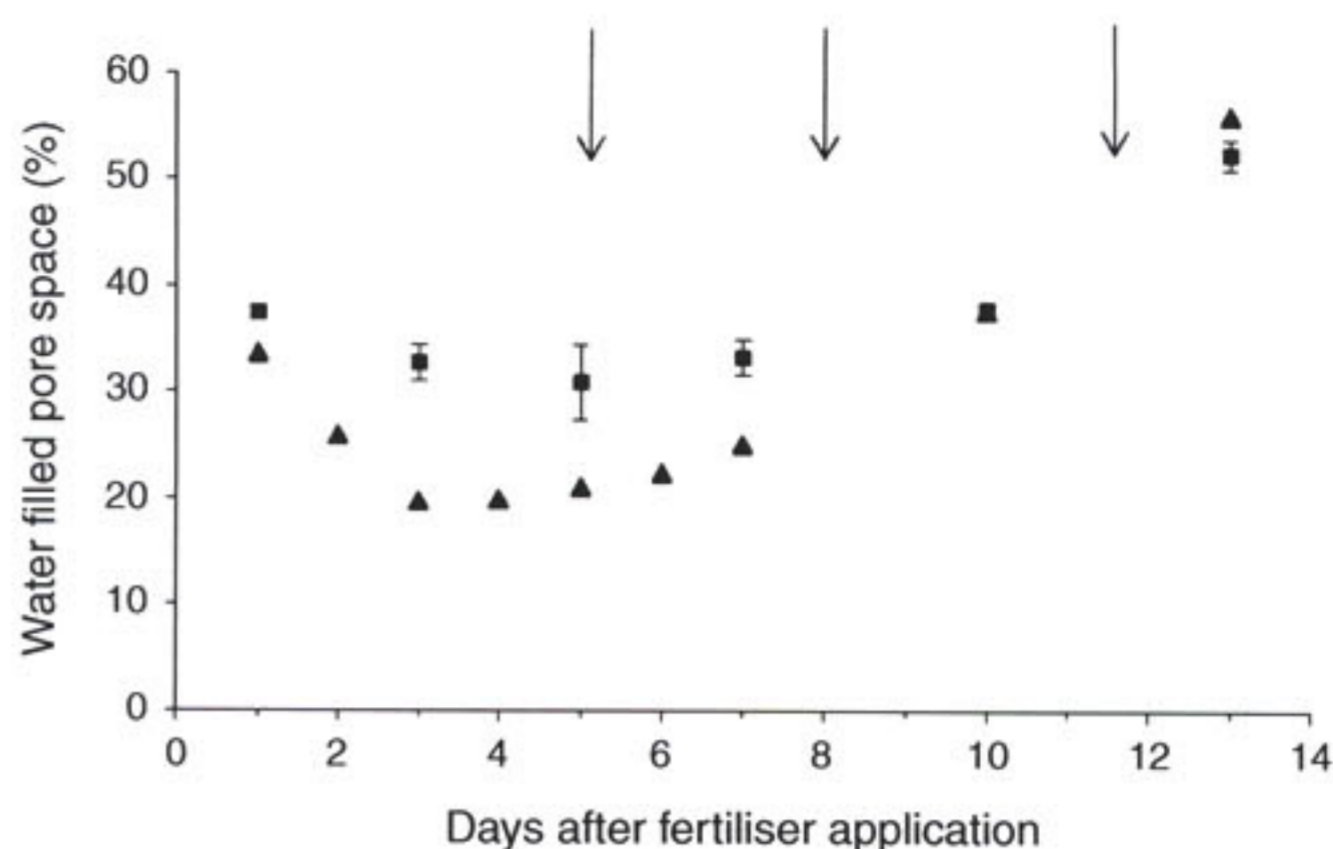


Fig. 1. Water-filled pore space in the 0–0.05 m (▲, one replicate) and 0–0.15 m (■, three replicates) soil layers during the experimental period. Vertical bars represent standard errors for the 0–0.15 m samples. Arrows denote rainfall events on days 5, 8, and 12 after fertilisation (3.9, 3.5, and 11.7 mm, respectively).

these low soil water contents, nitrification seems to be the dominant factor controlling the formation of NO, whereas denitrification is important at higher soil moisture contents (Hall *et al.* 1996; Ludwig *et al.* 2001).

The rainfall at 5, 8, and 12 DAF of 13.9, 3.5, and 11.7 mm, respectively, was only sufficient to significantly change the water content of the soil in the 0–0.15 m layer of the soil at 7, 10, and 13 DAF, and the 0.15–0.30 m layer at 13 DAF (results not shown). As nitrate moves with the water, it is unlikely that nitrate was leached further than the 0.15–0.30 m layer by the rainfall.

The urea and mineral N concentrations in the soil samples taken at 0.15-m depth intervals (three replicates) were extremely variable, which might be expected considering the method used for applying the urea and the number of people engaged in the application. Consequently, the analyses for the samples taken at 0–0.05 m (15 locations, one replicate) are presented to illustrate the trends in urea and mineral N concentrations during the study. Some of the applied N would have been taken up by the maize plants during the study and this would have affected the trends and amounts of urea, NH₄⁺, and NO₃[−] in the soil. It is apparent that there was sufficient water for urea hydrolysis to occur, and the concentration of urea in the 0–0.05 m soil layer decreased from ~804 μg N/g (calculated from the rate of urea application) to 38 μg N/g at 7 DAF (Fig. 2). Most of the urea had been hydrolysed by 13 DAF.

Prior to fertiliser application, the NH₄⁺ concentration in the surface soil layer was 6.3 μg N/g. The NH₄⁺ concentration in the 0–0.05 m layer increased to 85 μg N/g at 3 DAF and was still high (76 μg N/g) at 7 DAF (Fig. 3). The results for the 0–0.15 m layer were extremely variable but they, too, showed that the NH₃ concentration remained high until ~10 DAF. Therefore, there was a potential source in the surface soil for NH₃ volatilisation over a long period. While some of the NH₄⁺ produced is lost, and some is immobilised in the soil or taken up by the maize crop, the relatively high concentration remaining suggests that the rate of nitrification in this soil during our measurements was low.

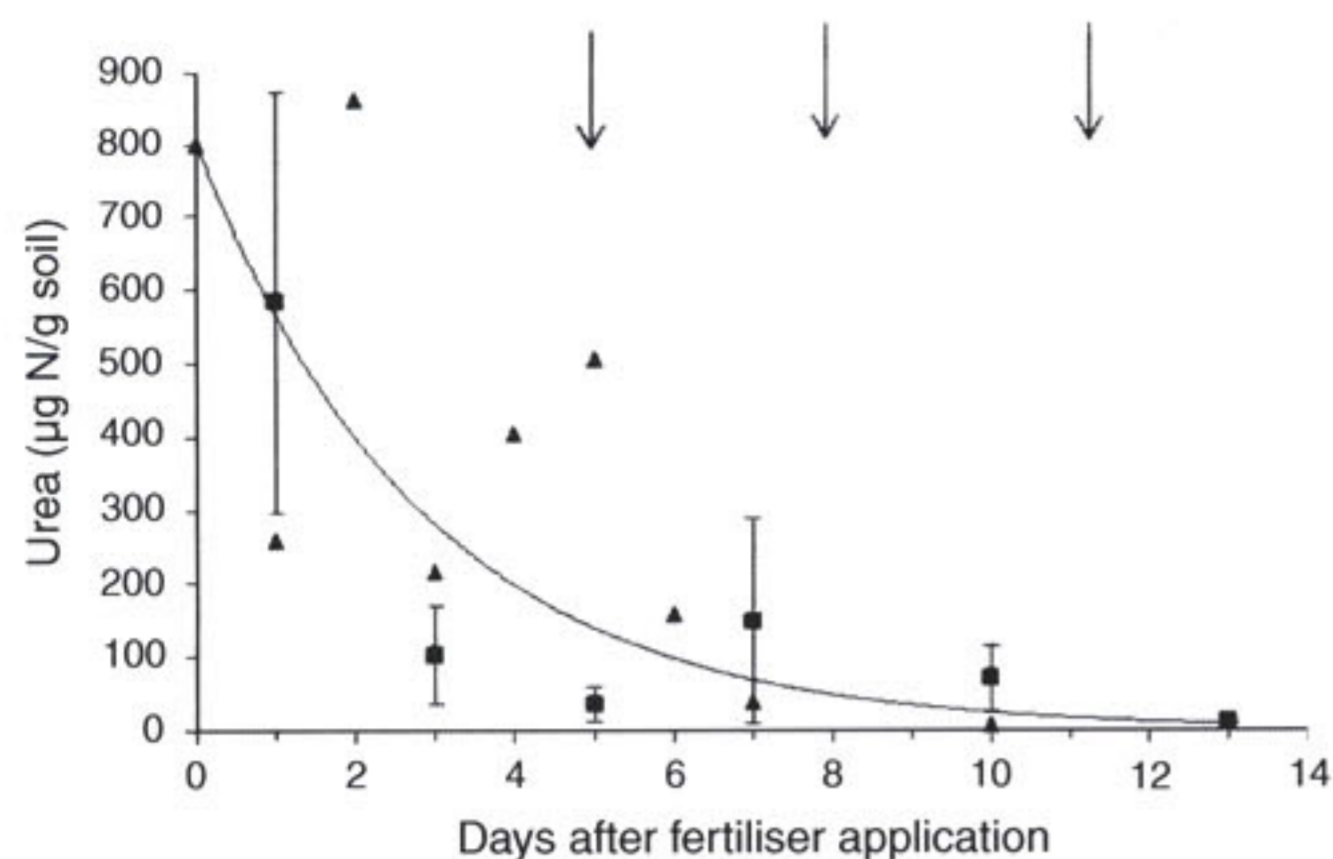


Fig. 2. Urea concentration in the 0–0.05 m (▲, one replicate) and 0–0.15 m (■, three replicates) soil layers after fertiliser application. Vertical bars represent standard errors for the 0–0.15 m samples. Arrows denote rainfall events on days 5, 8, and 12 after fertilisation (3.9, 3.5, and 11.7 mm, respectively). The urea concentration in the 0–0.05 m layer declined exponentially with time: $y = 804e^{-365x}$; $R^2 = 0.720$; $P < 0.01$; $n = 10$.

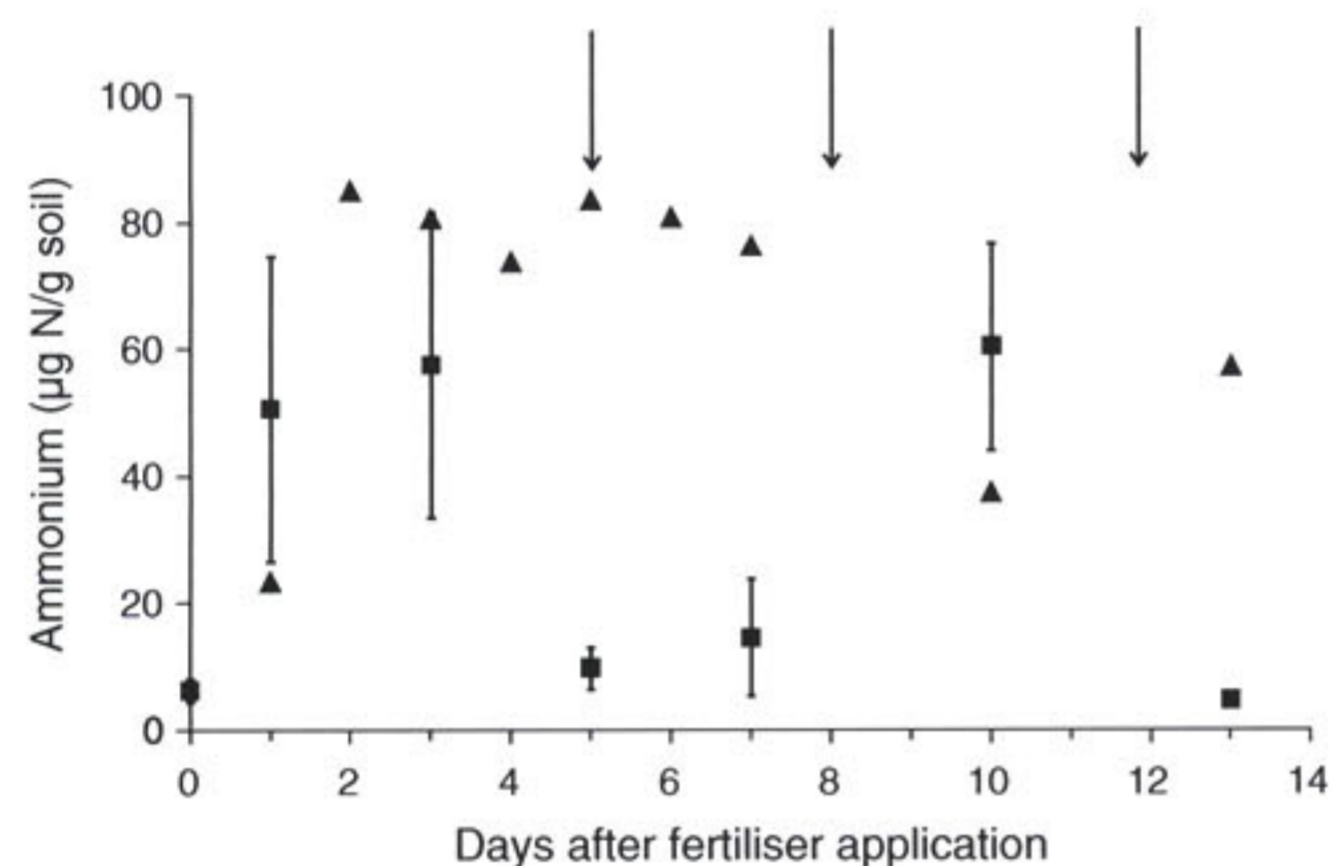


Fig. 3. Ammonium concentration in the 0–0.05 m (▲, one replicate) and 0–0.15 m (■, three replicates) soil layers after urea addition. Vertical bars represent standard errors for the 0–0.15 m samples. Arrows denote rainfall events on days 5, 8, and 12 after fertilisation (3.9, 3.5, and 11.7 mm, respectively).

The NO_3^- concentration in the surface soil was $5.1 \mu\text{g N/g}$ before fertiliser application. After the addition of urea, the NO_3^- concentrations in the soil samples of 0.15-m layers was extremely variable, but the highest value ($24.1 \mu\text{g N/g}$) was

measured at 10 DAF (Table 1). In the 0–0.05 m samples, the NO_3^- concentration fluctuated between 3.3 and $31.4 \mu\text{g N/g}$, and the maximum NO_3^- concentration found ($31.4 \mu\text{g N/g}$) was only 3.9% of the fertiliser N added.

Denitrification

Incubation of the soil samples with acetylene and sampling of the head space after 2 h produced very low and variable denitrification fluxes (results not presented). On the other hand, the results obtained after 6 h of incubation were much more consistent. It has been shown by Aulakh *et al.* (1991) that changes in denitrification rates coincided with changes in temperature, but were out of phase by 1–2 h. The poor results with the 2-h incubation may be due to the lag period between the outside temperature and denitrifying activity in the soil, or to a delay in acetylene diffusion into, or N_2O out of, the soil.

Denitrification rates were low ($0\text{--}104 \text{ g N}_2\text{O/ha.day}$) and variable (Table 2). However, it appeared that most of the denitrification took place in the 0–0.15 and 0.15–0.30 m layers of soil and little denitrification occurred in the other layers (Table 2). The rate of denitrification appeared to increase towards the end of the experimental period (10–13 DAF) as the WFPS increased due to heavy rain. The results suggest that $\sim 0.48 \text{ kg N/ha}$ was lost from the experimental area by denitrification during the study. As the WFPS was always $< 80\%$ (the critical level for denitrification; Linn and Doran 1984), it is not surprising that denitrification was not an important loss process in this experiment.

Respiration rates were measured in each of the soil samples of 0.15-m layers, and the results (not presented) showed that CO_2 was produced at all depths on all sampling occasions. The rates of production varied from 0.96 to $6.01 \text{ kg CO}_2\text{/ha.day}$, similar to those observed by Kowalenko *et al.* (1978) for a clay loam ($6.2 \text{ kg CO}_2\text{/ha.day}$) and a sandy soil ($3.3 \text{ kg CO}_2\text{/ha.day}$). The respiration rates tended to decrease with time, but there was no significant decrease in respiration rates with depth; for example, the respiration rates in the 0–0.15 m layers were not significantly different from those in the 0.60–0.75 m layers on all sampling occasions.

Denitrification in soil is determined by aeration (or water content), NO_3^- concentration, organic carbon, temperature, and availability of microorganisms (Tiedje 1988). In the subtropical zone it is unlikely that temperature was limiting (even in the subsurface horizons); thus, the low denitrifying activity at depth may have been due to a deficiency of NO_3^- , available carbon, or denitrifying organisms in the lower horizons. The results show

Table 1. Nitrate concentrations ($\mu\text{g N/g soil}$) at various depths and times after application of urea (60 kg N/ha) Means followed by the same letters are not significantly different at $P = 0.05$: upper case letters, rows; lower case letters, columns

Depth (m)	Days after fertilisation					
	1	3	5	7	10	13
0–0.15	5.07 ABCb	22.66 ABa	3.67 BCb	4.13 BCb	24.1 Aa	2.32 Cb
0.15–0.30	5.32 Ab	6.46 Ab	3.78 Ab	2.97 Ab	4.79 Ab	3.96 Ab
0.30–0.45	6.00 Ab	6.11 Ab	3.39 Ab	3.41 Ab	5.61 Ab	4.11 Ab
0.45–0.60	5.74 Ab	5.48 Ab	4.10 Ab	4.26 Ab	6.55 Ab	4.31 Ab
0.60–0.75	5.31 Ab	4.65 Ab	3.86 Ab	4.57 Ab	5.96 Ab	5.25 Ab

Table 2. Effect of soil depth and time on denitrification rates ($\text{g N}_2\text{O/ha.day}$) after application of urea (60 kg N/ha) Means followed by the same letters are not significantly different at $P=0.05$: upper case letters, rows; lower case letters, columns

Depth (m)	Days after fertilisation					
	1	3	5	7	10	13
0–0.15	1.14 Ab	6.84 Ab	7.04 Aab	11.02 Aa	57.30 Aa	103.50 Aa
0.15–0.30	0 Bb	55.40 Ab	13.04 Aa	7.57 Aab	30.67 Aa	1.50 Aa
0.30–0.45	8.41 Ab	1.96 Ab	0.05 Ab	2.45 Aab	10.58 Aa	2.92 Aa
0.45–0.60	0 Bb	1.27 Ab	0.23 Ab	0.12 Ab	1.10 Aa	1.54 Aa
0.60–0.75	0 Bb	0.13 Bb	0 Bb	0.11 Bb	2.52 Aa	1.06 ABa

that there was some NO_3^- in the lower horizons (Table 1), which most likely came from previous fertiliser applications as there is no evidence for nitrate leaching in this experiment. In addition, the respiration rates suggest that there was microbial activity in the lower horizons. The results therefore suggest that available carbon may have been the main factor controlling denitrification at depth.

Ammonia loss

Ammonia volatilisation is controlled by wind speed, temperature, and ammoniacal N concentration and pH in the surface soil (Sherlock *et al.* 1995). Wind speeds (at 1.5 m height) ranged from 0.13 to 5.0 m/s and averaged 1.65 m/s during the experimental period. Wind speeds were very low ($\sim 1 \text{ m/s}$) for long periods between 1 and 7 DAF and at 10 DAF. The air temperature varied from 21 to 42°C (average 33.1°C) during the experiment, with temperatures in the period up to 5 DAF being higher than those after that time. The pH of the unfertilised soil was high (8.5) and the alkalinity of the soil in the vicinity of the urea prills would have increased after urea hydrolysis so that some of the ammoniacal N would have been in the NH_3 form, with the potential to be lost (Sherlock *et al.* 1995). However, placement of the urea below the soil surface would have ensured that the ammoniacal N concentration at the soil surface was low and NH_3 would have had to diffuse to the soil surface before any loss could occur.

Some diffusion obviously occurred, as NH_3 was lost, but overall loss rates were low. Very little NH_3 was lost until 2 DAF (Fig. 4) and the rate of loss increased from $\sim 0.1 \mu\text{g N/m}^2.\text{s}$ at 3 DAF to $2.3 \mu\text{g N/m}^2.\text{s}$ at 5 DAF (Fig. 4). Loss rates then gradually decreased until 8 DAF, when the rate of loss increased to $1.8 \mu\text{g N/m}^2.\text{s}$. Loss rates were again reduced by the rain late on 8 DAF. The variation in loss rates after 5 DAF seems to be due to changes in wind speed and temperature. As shown in other studies (e.g. Sherlock *et al.* 1995), NH_3 loss rates were positively correlated with wind speed ($r=0.602$). At 8 DAF, it appeared that higher wind speeds ($\sim 4 \text{ m/s}$) and temperatures ($\sim 38^\circ\text{C}$) combined to produce a faster loss rate.

As can be seen in Fig. 4, some data were lost due to power failure and malfunction of the NH_3 to NO converter. In order to estimate the loss of NH_3 over the whole experiment, missing data were estimated in two ways: as the averages of measured fluxes over periods of the same duration immediately before and after the missing ones, and by fitting a fifth-order polynomial function to a plot of measured fluxes against time after fertiliser application. The total NH_3 loss estimated by the first procedure was 3.9 kg N/ha , and by the second was 3.4 kg N/ha , which correspond to 6.5% and 5.6% of the N applied, respectively. The cumulative losses of NH_3 over the measuring period estimated by both procedures are shown in Fig. 5.

Although some NH_3 loss was still occurring at 10 DAF, it is evident from Figs 4 and 5 that the loss rate was small by that time. Given the heavy rainfall that commenced at 8 DAF and the

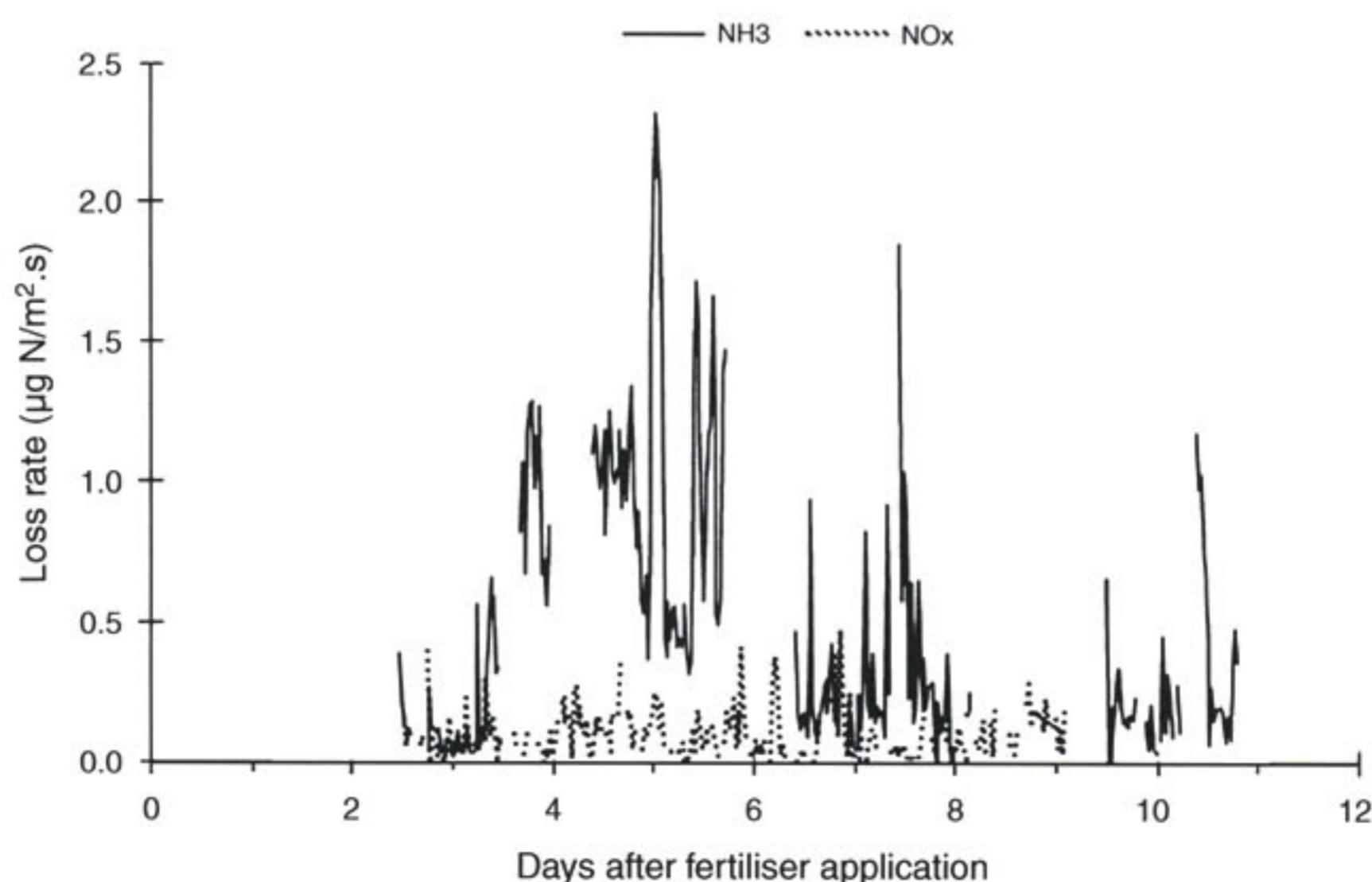


Fig. 4. Ammonia and NO_x emission following application of urea.

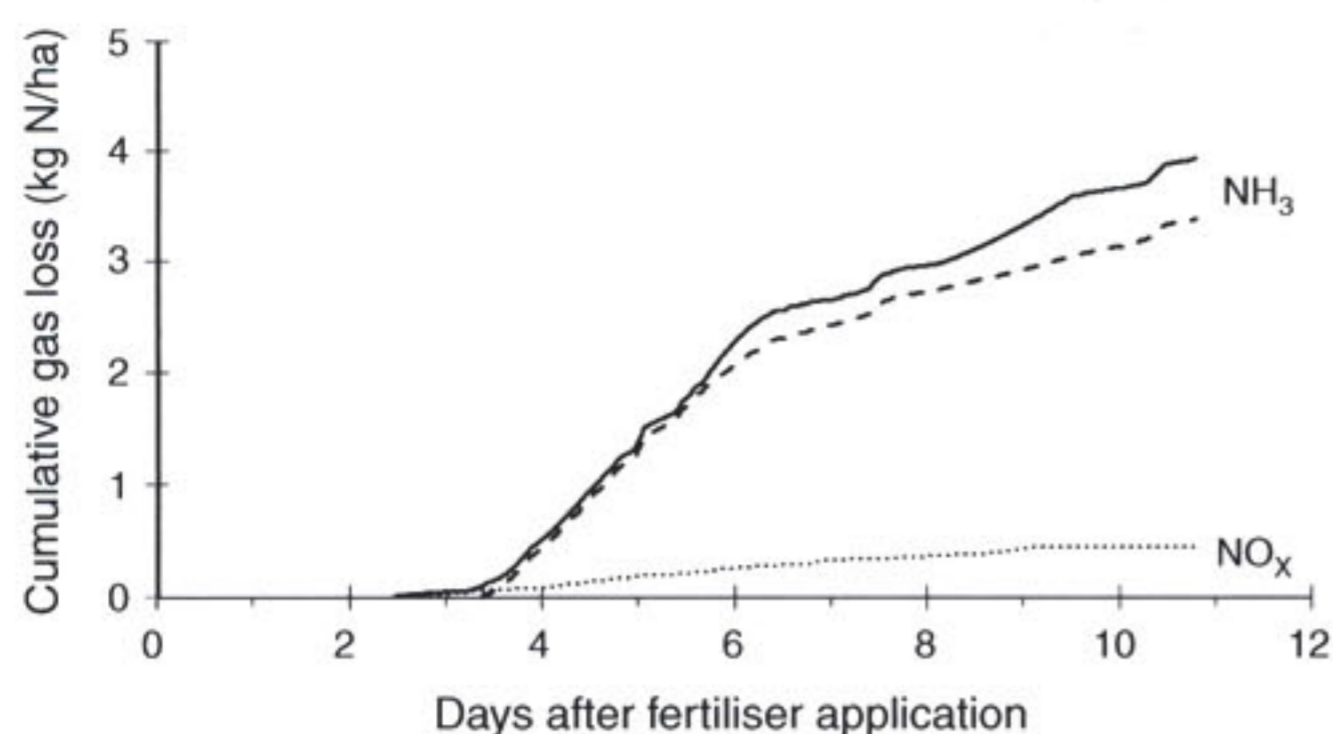


Fig. 5. Cumulative losses of ammonia and NO_x . Missing values for ammonia were estimated by linear interpolation (solid line) and by fitting a fifth-order polynomial function (dashed line). Missing values for NO_x (dotted line) were obtained by linear interpolation.

large reductions in urea and ammonium in the soil by that time or shortly afterwards (Figs 2 and 3), we expect that the overall loss would have been close to 4 kg N/ha, ~7% of the N applied. The emission pattern was remarkably similar to that observed by Prasertsak *et al.* (2002) in an investigation where urea was drilled into a freshly harvested sugarcane field (virtually bare soil) to a depth of around 0.05 m. Ammonia loss proceeded at rates somewhat $<1 \mu\text{g N/m}^2\cdot\text{s}$ until 50 mm of rain fell between 12 and 13 DAF. Following the rain, volatilisation increased to a rate of $\sim 2 \mu\text{g N/m}^2\cdot\text{s}$ at 15, 16, and 17 DAF and then ceased. Both urea and ammonium in the top 0.15 m of soil were also reduced to almost zero following the rain. The similarity of this emission pattern to our observations in the present investigation supports our assumption of negligible NH_3 loss 4 or 5 days after substantial rain.

Ammonia loss from applications of urea to maize crops has been studied at other sites on the North China plain (Zhang *et al.* 1992; Cai *et al.* 2002a, 2002b). Cai *et al.* (2002a, 2002b) showed that NH_3 loss varied from 11 to 48% of the N applied, depending on method of fertiliser application and environmental conditions. Ammonia losses were large (average 39%) when urea was broadcast onto the soil surface and smaller (average 14%) when the fertiliser was deep-placed. Similar results were obtained by Zhang *et al.* (1992). It is important to note that deep placement of urea reduces, but does not completely prevent, loss of NH_3 . Ammonia can be lost as a result of transport of NH_3 or NH_4^+ from deeper in the soil profile to the soil surface. Upward movement of NH_4^+ with evaporating water is possible (Ray *et al.* 1957; Fenn and Miyamoto 1981) and loss of NH_3 depends on the cation exchange capacity and texture of the soil. For example, in a fine-textured soil with high cation exchange capacity, very little NH_3 (0.9% of applied N) was lost from a subsurface application (Denmead *et al.* 1977).

The total loss of ~7% of applied N in the current experiment was much lower than observed in other experiments with deep placement on the North China Plain (average 14% loss, Cai *et al.* 2002a, 2002b; 12% loss, Zhang *et al.* 1992). The greater losses in those experiments may have been due to the higher rates of fertiliser application, which resulted in higher ammoniacal N concentrations. Other factors such as soil texture or cation exchange capacity may have contributed to the differing loss rates.

NO_x loss

Rates of loss of NO_x varied throughout the day and throughout the experimental period (Fig. 4) and averaged $0.1 \mu\text{g N/m}^2\cdot\text{s}$. Emission increased to a maximum of $0.5 \mu\text{g N/m}^2\cdot\text{s}$ at 7 DAF. Few data for NO_x emission were missed and these were estimated by the first procedure used for NH_3 , i.e. linear interpolation. The estimated total loss of NO_x during the study was 0.7 kg N/ha (Fig. 4), equivalent to 1.2% of the applied N.

Using automated chambers, Liu *et al.* (2010) measured NO emission from an application of urea (66.3 kg N/ha) to an adjacent, irrigated cotton field between 1 January and 31 December 2008. They found that emission of NO throughout the year varied from -3.7 to $135.7 \mu\text{g N/m}^2\cdot\text{h}$ (-0.001 to $0.038 \mu\text{g N/m}^2\cdot\text{s}$) and that 0.24% of the applied N was lost as NO. Liu *et al.* (2010) found that the maximum emission ($0.038 \mu\text{g N/m}^2\cdot\text{s}$) occurred in July, at the time of our measurements. This is considerably lower than the maximum recorded in our study. Their lower value may have resulted from the addition of 184.2 mm water to their plots after fertiliser addition and the higher WFPS (Ludwig *et al.* 2001).

The NO_x loss in our study is greater than the fertiliser-derived emission derived by Liu *et al.* (2010) and others. Veldkamp and Keller (1997) evaluated measurements obtained with different fertilisers, soils, and climates and concluded that, on average, 0.5% of fertiliser N was emitted as NO_x . Stehfest and Bouwman (2006) summarised 189 emission measurements for agricultural fields and developed a statistical model to simulate NO_x emission from soil, taking into account the influence of factors such as N application rate, soil N content, and climate. They concluded that, on average, 0.55% of the N applied to crops would be emitted as NO_x . Yan *et al.* (2005), using a similar technique, arrived at a value of 0.7%. The higher values obtained in the current study more likely reflect the true situation, as they were obtained continuously with a micrometeorological technique rather than spot measurements with chambers (Veldkamp and Keller 1997). Low frequency measurements may miss main emission events; for example, Liu *et al.* (2010) compared the total loss of nitrous oxide from a fertilised cotton crop determined by continuous measurement with those determined using spot measurements and found that the total losses could differ by as much as 70.5%.

Nitric oxide is produced in soils by both chemical and biological processes (Chalk and Smith 1983). When alkaline-hydrolysing fertilisers are added to soils, nitrite can accumulate because free NH_3 from the fertiliser inhibits the oxidation of nitrite to NO_3^- . When the nitrite decomposes chemically, NO is formed (Chalk and Smith 1983). Nitric oxide is also produced as a by-product of the microbial processes nitrification and denitrification (Hall *et al.* 1996; Francis *et al.* 2008). Some workers (e.g. Dunfield and Knowles 1999; Göttsche and Conrad 2000; Venterea and Rolston 2000) found that nitrification was the dominant process for NO production, whereas others attribute the production of NO to denitrifier activity (e.g. Cárdenas *et al.* 1993). The dominant factor controlling the formation of NO seems to be the moisture content of the soil, with nitrification being the important process at low moisture contents and denitrification important at high moisture contents. While a high soil water content favours denitrifier activity, it restricts NO transport through the soil and enhances the

probability that NO will be further metabolised by the denitrifiers.

Ludwig *et al.* (2001) showed that optimum moisture content for NO production was 20% WFPS, and Remde and Conrad (1990) found that nitrifiers were responsible for NO production in an alkaline soil whereas denitrification was the dominant process in an acidic soil. Although the relatively constant NH_4^+ concentrations in the surface soil until 10 DAF and the low NO_3^- concentrations indicate that nitrification was very slow, the low values for WFPS until rain fell at 10 DAF and the alkalinity of the soil suggest that NO was formed mainly by nitrification. However, the results of the denitrification study suggest that denitrification was also occurring in the surface soil, presumably in anaerobic microsites. Thus, production of NO during denitrification cannot be ruled out.

Conclusions

This study, using micrometeorological techniques, showed that 7% of the applied N was lost by NH_3 volatilisation when the urea fertiliser was deep-placed using farmers' local practice, and that 1.2% of the applied N was lost as NO_x . It appears that the nitrification rate in this soil was low, because the NH_4^+ concentration in the surface soil was relatively constant until 10 DAF, and the maximum amount of NO_3^- found in the soil was only 3.9% of the fertiliser N added. Thus, there is little potential for NO_3^- to be leached down the profile. The study using soil cores and acetylene inhibition to measure denitrifying activity suggests that the rate of denitrification was also very low in this soil until after heavy rain at 10 DAF. The results indicate that in this soil where nitrification and denitrification rates are low, and there is little potential for NO_3^- to be leached, deep placement of the urea to limit NH_3 volatilisation will improve the efficiency of fertiliser use. The results also indicate that the concern expressed by McElroy and Wang (2005) about the validity of results for NO_x and NH_3 emission from agriculture is warranted. The measured NO_x loss in this study is far greater than the fertiliser-derived emission measured by others, and the results for NH_3 show that, even though the fertiliser was placed below the soil surface, NH_3 is still lost to the atmosphere. However, the extent of loss in the current experiment was only about half of that observed in other experiments with deep placement on the North China Plain. The greater losses in those experiments may have been due to the higher rates of fertiliser application, which resulted in higher ammoniacal N concentrations.

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