Loss of nitrogen by ammonia volatilization and NOx emission after application of urea to irrigated maize in Shanxi Province, China

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Abstract
An experiment, using emerging micrometeorological techniques, was conducted on a urea fertilized maize crop in Shanxi Province in northern China to determine the importance of ammonia volatilization and NO_x emission as indirect greenhouse gases. The results showed that 6% and 1.2% of the applied N was lost as ammonia and NO_x, respectively.

Key Words
Nitrification, denitrification, backward Lagrangian dispersion.

Introduction

Most of the maize produced in China is grown in the northern part of the country (~70% of the total area planted) where yields in the last 50 years have increased from 1180 kg/ha to 5000 kg/ha mainly as a result of the application of fertilizer nitrogen (N) (Zhen *et al*. 2006). However, due to the lack of direction many farmers have applied too much fertilizer which has resulted in low N use efficiency (Goa *et al.* 2009). The reason for the low efficiency is that much of the N applied is lost from the plant-soil system by ammonia (NH_3) volatilization, during nitrification, and by leaching, erosion, runoff, and denitrification (Yan *et al*. 2003; Zhu and Chen 2002). The N may be lost as NH_3, nitrogen oxide and nitrogen dioxide (collectively referred to as NOx), the greenhouse gas nitrous oxide (N_2O) and dinitrogen, and the amounts lost are influenced by the ecosystem, soil characteristics, cropping procedure, fertilizer techniques, and prevailing weather conditions. While not regarded as greenhouse gases, NH_3, and NO_x, play important roles in the greenhouse story through the formation of secondary aerosols which affect the earth's radiation balance. As the formation of secondary aerosols is expected to have significant effects on the variability and intensity of the Asian Monsoon (MAIRS 2008) it is important that reliable data are available for assessing the impact of increased fertilizer N use on the emission of these gases. The accuracy of the values obtained for NH_3 and NO_x emission from monsoon Asia have been questioned (Wang *et al.* 2004; McElroy and Wang 2005). The values obtained for NO_x emission from soil are uncertain (Yan *et al.* 2005) and one reason may be that most have been obtained as spot measurements with chambers (Veldkamp and Keller 1997). Consequently an experiment was conducted on a urea fertilized maize crop in Shanxi Province in northern China to determine the importance of NH_3 volatilization and NO_x emission using the best available emerging micrometeorological techniques.

Material and methods

The experiment was conducted in a farmer's field at Yongi, Shanxi Province, China in July 2008. The cultivated horizon (0-20 cm) of the soil at the site contained 16.6% sand, 46% silt and 37.4% clay. It had a pH (1 soil: 5 water) of 8.5 and contained 9.6 g/kg organic C, 1.09 g/kg total N, 6.3 µg N /g soil as ammonium and 5.1 µg N /g soil as nitrate. The bulk density of the soil was 1.23 g cm^3. Maize (variety Nongda 108) was seeded on June 6 after harvesting wheat. Prilled urea (60 kg N/ha) was applied by the traditional point deep placement technique at a depth of 5-10 cm on July 9 (33 days after seeding) between 0900-1100, and 1600-1830. The technique used by the farmer involved removal of a small amount of soil to the required depth with a hoe, addition of a calculated amount of urea to the hole by hand and covering the urea with soil.

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 from 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 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 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

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

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

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

where C_b is the background (upwind) concentration. The calculations required to evaluate Eq. (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 interactive 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 were measured with a 3-D sonic anemometer (Campbell Scientific CSAT-3) installed in a neighbouring maize field. Ammonia concentrations were measured with a chemiluminescence analyser (Model EC9842T; Ecotech, Melbourne, Australia) installed near the centre of the fertilized plot and sample lines (6 mm diameter polyethylene tubing) were run to the analyser from intake points at the plot centre and 10 m upwind of the plot boundary. Measurements of NH_3 concentrations were made initially at 1.5 m above the ground increasing to 2 m as the crop grew. The same analyser was used to determine the concentration of NO_x. The analyzer measures NO concentrations in the air stream directly and NO_2 concentrations after the stream has passed through a converter to change NO_2 to NO.

The fertilized area was divided into 3 blocks representing the western, central and eastern sections, and field moist soil samples were collected at intervals after fertilizer application using a soil corer with an external diameter 4.46 cm. Six replicate cores at depths of 0-15, 15-30, 30-45, 45-60, 60-75 and 75-90 cm were taken from each block and the individual layers were combined for analysis. On each occasion 10 g moist soil was extracted with 20 mL of 2 M KCl containing 5 mg/L phenylmercuric acetate solution for determination of urea, ammonium, and nitrate. Urea in the soil extracts was determined using a modified diacetymonoxime method (Mulvaney and Bremner 1979), and ammonium and nitrate were determined by a colorimetric procedure using a Technicon Autoanalyser (Rayment and Higginson 1992). The denitrification rates at the six different depths in the soil were determined by an acetylene inhibition method (Aulakh *et al.* 1991).

Results and discussion

One day after fertilizer application (10 July), when 14 mm rain fell, the moisture content of the 0-15 cm surface soil was 16% and it decreased to 13.3% on 14 July. Following rain on 14, 17 and 21 July the moisture content increased to 22.4%. The water filled pore space decreased from 36.8 on 10 July to 30.4% on 14 July and increased to 51.5% on 22 July. After the rain on 10 July there was sufficient water for hydrolysis to occur and the concentration of urea decreased rapidly from 585 to around 100 µg N/g soil on 12 July and remained at that level until 19 July. Most of the urea had been hydrolyzed by 22 July. The ammonium concentration increased from 6.3 to ~74 µg N/g soil on 10 July and remained high until 19 July. By 22 July the ammonium concentration had decreased to 5 µg N/g soil. The nitrate concentration increased from 5.1 to 9.6 µg N /g soil on 10 July and remained close to 9 µg N /g soil throughout the experimental period. The relatively constant ammonium concentrations and low values for nitrate up to 19 July suggest that the nitrification rate in this soil was slow. The denitrification rates determined by the procedure of Aulakh et al (1991) were low (range 2.9 to 115.9 g N_2O /ha/day) in line with the low water filled pore space (well below the 80% critical level for denitrification, Linn and Doran 1984). Denitrification varied with time and depth in the soil profile, but in general most of the denitrification took place in the 0-15 cm surface layer of soil. The rate of denitrification increased towards the end of the experimental period when the water filled pore space increased due to heavy rain.

Ammonia loss

Overall NH_3 loss rates were slow and very little NH_3 was lost until 2 days after rain fell on 10 July (Figure 1). Ammonia volatilization is controlled by pH and the ammoniacal N concentration in the surface soil, temperature and wind speed (Sherlock *et al*. 1995). The pH of the unfertilized soil was high (8.5) and this would have been increased in the vicinity of the urea prills after urea hydrolysis so that some of the ammoniacal N would have been in the NH_3 form with the potential to be lost. However, placement of the

urea below the soil surface would have ensured that the ammoniacal N concentration at the soil surface would have been low and NH_3 would have had to diffuse to the soil surface before any loss could occur. Some diffusion obviously occurred and the rate of loss increased from ~0.1 µg N/m^2/s on 12 July to 2.3 µg N/m^2/s on 14 July (Figure 1). Loss rates then gradually decreased until 17 July when the rate of loss increased to 1.8 µg N/m^2/s. Loss rates were again reduced by the rain late on 17 July. The variation in loss rates after 14 July seems to be due to changes in wind speed and temperature. On 17 July the higher wind speeds (~4 m/s) and temperatures (~38°C) combined to produce a faster loss rate. The total loss of 6% of the applied N was much lower than the 11-12% loss observed in other experiments with deep placement on the North China Plain (Zhang *et al*. 1992; Cai *et al*. 2002). The higher losses in those experiments may have been due to the higher rates of fertilizer application.

NO_x loss

The rates of loss of NO_x varied throughout the day and throughout the experimental period (Figure 1) and averaged 0.1µg N/m^2/s. Emission commenced at a slow rate on 12 July and increased gradually to a maximum of 0.5 µg N/m^2/s on 16 July. The total loss of NO_x during the experiment was 1.2 % of the applied N. This is far greater than the fertilizer derived emission derived by others. Veldkamp and Keller (1997) evaluated measurements obtained with different fertilizers, soils and climates and concluded that on average 0.5% of fertilizer N was emitted as NO_x. Stehfest and Bouwman (2006) summarized 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 calculated the fertilizer induced emission from soil to be 0.55% of the nitrogen applied. Yan et al (2005) using a similar technique arrived at a value of 0.7%.

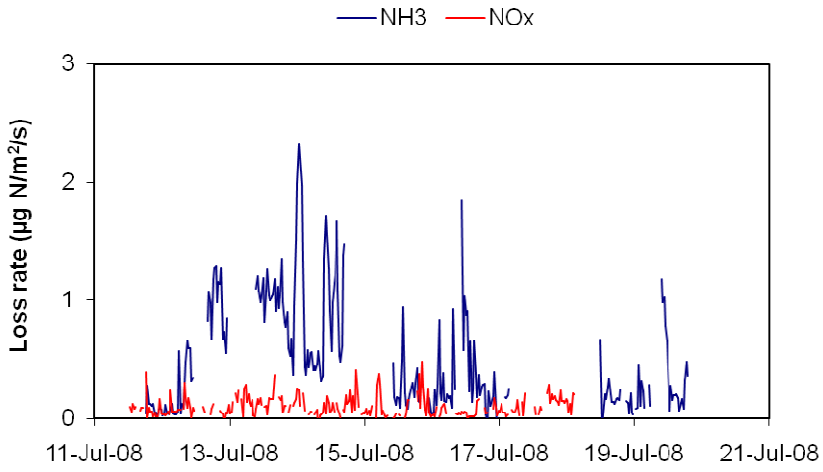

Figure 1. Ammonia and NO_x emission following application of urea to maize in China.

NO_x can be produced in soil as a by-product of nitrification and denitrification, but at low water filled pore space it is generally accepted that nitrification is the important process (Ludwig *et al*. 2001). As the water filled pore space in this study was between 30% and 37% until rain fell on 19 July it might be assumed that NO_x was formed mainly by nitrification. The relatively constant ammonium concentrations in the surface soil for the first 10 days after fertilization and the low nitrate concentrations indicate that nitrification, while slow, did occur. However, the results of the denitrification study suggest that denitrification was also occurring in the surface soil, presumably in anaerobic microsites. Consequently we are not able to determine the mechanism for the production of the NO_x in this study.

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