Effect of water addition and the urease inhibitor NBPT on the abatement of ammonia emission from surface applied urea

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ABSTRACT

Urea is considered the cheapest and most commonly used form of inorganic N fertiliser worldwide. However, it has been estimated that 5–30% of the urea N is lost as volatilised NH_3. Implementation of NH_3 mitigation strategies is crucial in order to reduce both the economic and environmental impact associated with NH_3 losses from urea application. Urease activity inhibitors and water addition to the soil have been proposed by UNECE (i.e. Gothenburg Protocol) as means to reduce NH_3 emission from fertiliser applications. In this study, two field experiments were carried out in order to test the effectiveness of water addition as NH_3 mitigation technique from surface applied urea in comparison with the use of the urease inhibitor NBPT. A system of wind tunnels was used to measure NH_3 fluxes. Contrasting irrigation strategies (or rainfall patterns), in terms of both rate and timing, were used in order to evaluate the amount of water necessary to achieve a significant NH_3 mitigation. The addition of 7 and 14 mm of water to the soil, immediately after urea spreading, reduced NH_3 emission by 77 and 89%, respectively, similar to that achieved using NBPT (77–88% reduction). In contrast, a simulated 3 mm rainfall, immediately after fertilising, significantly enhanced NH_3 volatilisation (with an 8% increase in emission compared to urea application without water addition). These results demonstrate the potential of correct water management in abating NH_3 volatilisation from urea applications to soil, giving a similar effect to that of the urease inhibitor NBPT under the experimental conditions presented here.

1. Introduction

Since the invention of the Haber–Bosch process in 1908, through which ammonia (NH_3) can be synthesised from atmospheric nitrogen (N_2), the use of synthetic N fertilisers has become common in many parts of the world (Erisman et al., 2007). Among the different forms of synthetic N fertilisers applied nowadays, urea is considered the cheapest and most commonly used form of inorganic N fertiliser (Thompson and Meisinger, 2004), accounting for c. 50% of total inorganic N use. However, it has been estimated that between 5 and 30% of the urea N is lost as volatilised NH_3 (UNECE, 2001; Erisman et al., 2007). Bouwman et al. (1997) estimated that, from the 78×10^9 kg of inorganic N applied globally (1995), 14% is lost as NH_3, with 65% of that amount lost from urea application. In a direct way, these losses of NH_3 are responsible for an important decrease in the nutrient value of the applied urea (Van der Stelt et al., 2005). In addition, emissions of NH_3 to the atmosphere can contribute to particulate matter formation affecting human health and to eutrophication and acidification of aquatic and terrestrial ecosystems after deposition (Erisman et al., 2007).

Since most of the NH_3 emission from the use of synthetic fertilisers comes from urea, it represents a priority area for the development of potential mitigation techniques. According to the advisory code of good agricultural practices by the Expert Group on Ammonia Abatement (UNECE, 2001), mitigation of NH_3 emissions from urea application can be achieved by a) specific measures based on incorporating it into the soil, b) applying it during appropriate weather conditions and c) the use of urease inhibitors (UNECE, 2001). The first two options are mainly focussed on enhancing the contact between ammonium (NH_4^+) and the soil colloid in such a way that NH_3 would be decreased in the soil solution. Addition of water to the soil surface, through rainfall or irrigation, immediately after surface application of urea would be included in this group. The third option, based on the use of urease activity inhibitors, is a biochemical method which retards the hydrolysis of urea by inhibiting the urease enzyme in the soil (Gill et al., 1997). Slowing urea hydrolysis allows more time for urea to

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diffuse into the soil following application. Therefore, the concentration of NH_3 and NH_4^+ present in the soil solution near the surface is reduced, thus reducing the potential for volatilisation losses (Grant et al., 1996). Among the various types of urease inhibitors which have been identified and tested, N-(n-butyl) thiophosphoric triamide (NBPT) has been found significantly effective at relatively low concentrations under both laboratory (Carmona et al., 1990; Gill et al., 1997) and field conditions (Sanz-Cobena et al., 2008; Zaman et al., 2009). Under field conditions, the inhibitor is normally applied by including it in granules of urea, which may limit the proportion of microsites where the enzyme is inhibited. It forms stable complexes with urease and is among the most efficient inhibitors of this enzyme after the conversion to its oxidised form (NBPTO) in soil (McCarty et al., 1989; Manunza et al., 1999). As urease is an enzyme present in a wide variety of fungi and bacteria species of soil, the efficiency of NBPT to decrease urease activity may depend on its diffusion from the application point and the concentration of inhibitor maintained in microsites. Although there is little information about the effect of rainfall or irrigation on the efficiency of urease inhibitors, we hypothesised that water application (i.e. irrigation or rainfall), following fertilisation, could enhance the effect of NBPT in mitigating NH_3 emission. Alternatively, water application alone may prove an effective alternative mitigation technique and particularly appropriate where irrigation is routinely practised. However, there is limited information evaluating the effect of irrigation management on ammonia emission after urea application under field conditions, and in particular the effect of rate or frequency. The present study was conducted, therefore, to assess (1) the mitigation effect of the urease inhibitor NBPT with or without irrigation (or rainfall) on NH_3 emission and (2) the effect of different rainfall (or irrigation) patterns on NH_3 volatilisation after urea application.

2. Materials and methods

2.1. Experimental site

The experiment was conducted at North Wyke Research station in Devon, UK, on a clay loam soil (20% sand, 50% silt, 30% clay) of the Hallsworth (Stagnogley; USDA Haplaquept) series with a pH in water of 5.3, bulk density 0.99 g cm^{-3} and 3.7% of organic carbon (Findlay et al., 1984). Average annual rainfall at North Wyke is 1035 mm and average soil temperature (10 cm) 6 °C (min) and 13 °C (max).

2.2. Experimental design

Two experiments were conducted on a tilled area which had not previously been used by animals at North Wyke. The experimental area was selected and tilled on the 15th April 2008. Eighteen 2 m^2 plots were used for each experiment. The first experiment was conducted between the 21st April and the 6th May 2008 and the second one between the 12th May and the 27th May 2008, in an adjacent area to that of experiment 1 and without any management practice in the meantime. Initial soil conditions at the start of experiments were WFPS of 61.6% and 39.1% and soil NH_4^+ soil content of 2.1 and 2.5 mg NH_4^+-N kg^{-1}, for experiments 1 and 2, respectively, and bulk density of 0.99 g cm^{-3} for the two experiments.

Both experiments included 6 different treatments with 3 replications. Nine plots were fertilised with urea, used in granular form, and 9 with urea combined with the urease inhibitor NBPT (i.e. U + NBPT); both applied by hand at a rate of 100 kg N ha^{-1}. Urea was coated with the urease inhibitor NBPT shortly prior to application (as there was concern that the coated product may not be stable over the long-term), to give a proportion of inhibitor in the mixture of 0.14% on a weight basis. In each experiment, two different rainfall patterns

(i.e. rate and frequency) were simulated in order to test their effect on incorporating the fertiliser into the soil and, therefore, reducing NH_3 losses through volatilisation. In the first experiment, rainfall pattern 1 consisted in irrigating plots with 7 mm of water immediately after applications (treatments U + 7; U + NBPT + 7) using a watering can. Rainfall pattern 2 was based on irrigating with 7 mm of water immediately following application and then with a further 7 mm one week later (treatments U + 7 + 7; U + NBPT + 7 + 7). Plots without water application were also included as control (treatments U and U + NBPT). Therefore, there were 6 different treatments (i.e. U; U + NBPT; U + 7; U + NBPT + 7; U + 7 + 7; U + NBPT + 7 + 7) with 3 replicates per treatment in a randomised block design.

The second experiment included two further rainfall patterns: applying 14 mm just after fertilising (treatments U + 14 and U + NBPT + 14), and 3 mm added immediately after application and followed by further 3 mm one week later (i.e. U + 3 + 3 and U + NBPT + 3 + 3). Again, plots without rainfall were used as control (treatments U and U + NBPT) as well as for evaluating the effect of different temporal conditions on the results of the two experiments. Therefore, experiment 2 included the following treatments: U; U + NBPT; U + 14; U + NBPT + 14; U + 3 + 3; U + NBPT + 3 + 3, with 3 replicates per treatment in a randomised block design.

Air and soil temperature (2 m height and 10 cm depth, respectively) and relative humidity were monitored by a meteorological station located at the field site using temperature probes. Following Sommer and Olesen (1991), it was assumed that the wind tunnel canopy had no significant influence on temperature at the emitting surface.

2.3. NH_3 emission measurement

A system of small wind tunnels, as described by Lockyer (1984) and evaluated by Van der Weerden et al. (1996) was used to measure NH_3 emissions from surface applied urea. This technique is commonly used to measure NH_3 emission from small experimental plots (e.g. 1 m^2) for comparative purposes (Loubet et al., 1999a; Génermont et al., 1998; Misselbrook et al., 2005a). Each tunnel comprised a transparent polycarbonate canopy measuring 2×0.5 m, coupled to a steel duct which housed an electrically driven fan and an anemometer so that air flow through the tunnel could be controlled (at 1 m s^{-1} in the present study).

Ammonia concentration in the air entering and leaving the tunnel was measured by drawing air at 4 l min^{-1} through absorption flasks containing 0.02 M solution of orthophosphoric acid. Absorption flasks consisted of conical flasks containing between 80 and 100 ml of acid solution, with air being drawn through the solution via an unscintered, open-ended glass rod (Misselbrook et al., 2005b). When the absorption flasks were returned to the laboratory the contents were made up to 100 ml with deionised water. Each sample was then stored in a 30 ml polystyrene vial in a cool room (<4 °C) until they were analysed for ammonium-N concentrations by automated colorimetry (Searle, 1984), with NH_4^+ detection limits of 0.10 and 1.08 mg N l^{-1} using the low (0–5 mg l^{-1}-water) and high ranges (0–50 mg l^{-1}-water), respectively. The loss of ammonia from beneath each tunnel for each measurement period was calculated as the product of air which flowed through the tunnel and the difference between the concentrations of NH_3 in the air entering and leaving the tunnel. Measurements continued for a period of 21 d, with absorption flasks being changed every 24 h.

Loss estimates in periods not measured (e.g. when absorption flasks were being changed) were made by averaging the rate of loss of the periods immediately before and immediately after the missing period and multiplying by the time. Tunnel canopies were placed covering the plot immediately following application of treatments and removed and then replaced again after irrigation.

2.4. Soil measurements

Soil cores (0–10 cm depth) were collected several times during the two experiments in order to analyse the evolution of soil NO_3^-, exchangeable NH_4^+, urease activity and soil moisture. Mineral N content (NO_3^--N and NH_4^+-N) was determined by extraction of 4 g of fresh soil with 50 ml 2 M KCl followed by automated colorimetry (Searle, 1984). Urease activity was determined following the method of Nannipieri et al. (1980), involving the incubation of soil with buffered urea solution, the extraction of NH_4^+ with 1 N KCl and colorimetric NH_4^+ determination. Urease activity of the experimental soil prior to fertilising was also determined.

Gravimetric soil moisture content was determined by drying samples to constant weight at 80 °C. Water-filled pore space (WFPS) was estimated by dividing the volumetric water content by total soil porosity. Total soil porosity was calculated by measuring the bulk density of the soil according to the relationship: soil porosity $= 1 - (\text{soil bulk density}/2.65)$, assuming a particle density of 2.65 Mg m^{-3} (Danielson and Sutherland, 1986).

2.5. Statistical analysis

Statistical analysis was performed using Statgraphics Plus 5.1 (Manugistics, 2000). The data distribution normality of the NH_3 fluxes and that of soil NO_3^-, NH_4^+ was verified using the Kolmogorov–Smirnov test. Differences between treatments were analysed using analysis of variance (ANOVA, $P < 0.05$). The least significant difference (LSD) test was used for multiple comparisons between means. For non-normally distributed data, the Kruskal–Wallis test was used on non-transformed data to evaluate differences at $P < 0.05$. Linear regression analyses ($P < 0.05$) were performed to determine relationships between NH_3-N fluxes with soil NH_4^+-N, NO_3^--N and urease activity.

3. Results

3.1. Experiment 1

3.1.1. Environmental conditions

Initial WFPS was higher than 60%, mainly due to precipitation on 21st and 22nd of April, which also enhanced the relative humidity of air (i.e. $\geq$80%). Soil moisture was affected by irrigation, increasing to 69% WFPS for the 7 mm irrigated soil for the 1st day and decreasing progressively to 47.7% a week after. The second 7 mm of water added enhanced soil moisture content in U + 7 + 7 and U + NBPT + 7 + 7 from 49.3 and 46.7% to 49.9 and 55.3%, respectively. In soils without any water addition, WFPS decreased from 66 to 49% and 65 to 41% over the measurement period for U and U + NBPT, respectively. Soil temperature (i.e. 10 cm depth) ranged between 9 and 12.5 °C over the experimental period.
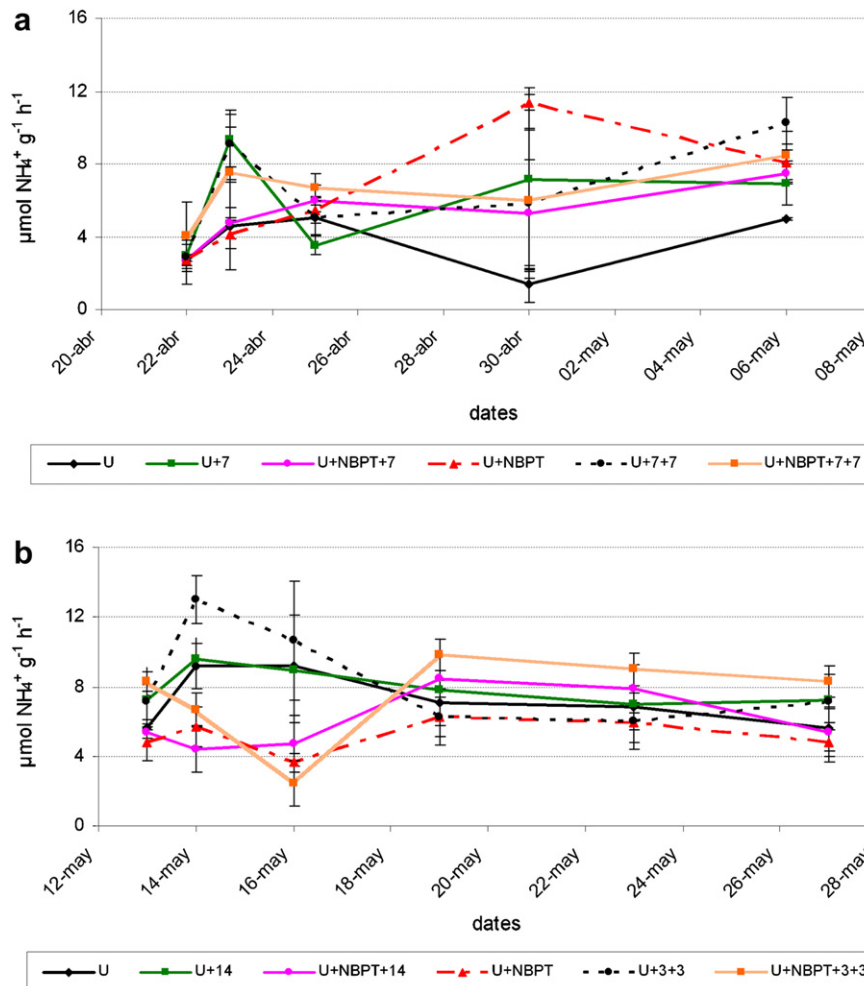

Fig. 1. Urease activity (μmol NH_4^+ g^{-1} h^{-1}) in the 0–10 cm soil layer in Experiments 1 (a) and 2 (b). Vertical lines indicate standard errors.

3.1.2. Evolution of mineral N and urease activity

Urease activity of all treated plots was similar immediately after fertiliser application. After 24 h, urease activity was lower in the NBPT treated plots than in those where the urea was applied without the inhibitor (Fig. 1a), with rates up to 8 μmol $NH_4^+ g^{-1} h^{-1}$ in the latter case. After 3 days, there was no significant difference in urease activity between treatments.

In those plots irrigated immediately after fertilising, urease activity remained constant (at c. 6 μmol $NH_4^+ g^{-1} h^{-1}$) for the duration of the experimental period. There was no effect of the 2nd simulated rainfall (i.e. 7 mm) on urease activity (Fig. 1a).

Exchangeable ammonium (NH_4^+) was affected by the presence of NBPT. Soil ammonium concentration (0–10 cm) was significantly higher for U soil than for other treatments immediately after fertilising, whereas no significant differences were observed in the exchangeable NH_4^+ between the other treatments. A progressive decrease in the pool of NH_4^+ was observed in all treatments except U + NBPT, without any irrigation, where increasing concentrations were measured (Fig. 2a). No significant differences in NO_3^- concentrations between the differently treated plots were measured within the experiment. Soil NO_3^- concentration increased over the experimental period in all treatments, with a peak value of 20.7 mg NO_3^--N kg^{-1} measured in the U + 7 soil. At the end of the experimental period, the treatments with the lowest NO_3^- concentration were U + NBPT and U (Fig. 3a).

3.1.3. Ammonia emission

Ammonia emission from U started to increase immediately after fertilising, peaking 48 h after application and declining to background levels after 7 d (Fig. 4a). No significant differences were found in NH_3 emission rate between U + 7 and U + 7 + 7 throughout the experimental period (Fig. 4a). Generally, the addition of water (i.e. 7 mm) resulted in an earlier peak in NH_3 emission (after 24 h), with the exception of U + NBPT + 7, where NH_3 emissions were lower than 0.5 kg N-NH_3 $ha^{-1} d^{-1}$ throughout the experiment.

Inclusion of NBPT with urea fertiliser, with no irrigation, significantly reduced the peak emission rate at 48 h (U + NBPT vs. U, Fig. 4a). With 7 mm irrigation, the effect of NBPT was less clear, as U + NBPT + 7 had the lowest emission rates, but U + NBPT + 7 + 7 had a higher initial emission rate (after 24 h) than either U + 7 or U + 7 + 7 (Fig. 4a).

Highest cumulative NH_3 emission over 12 d was from U (31.4 ± 5.8 kg N ha^{-1}, 31% of N applied), followed by U + NBPT + 7 + 7 (11.9 ± 0.9 kg N ha^{-1}). The treatment producing the lowest emissions was U + NBPT + 7 (3.2 ± 0.7 kg N ha^{-1}). No significant differences were found between the other treatments (Table 1).

3.2. Experiment 2

3.2.1. Environmental conditions

Initial soil moisture was lower than in the previous experiment. Immediately after placing the tunnel canopies, WFPS ranged
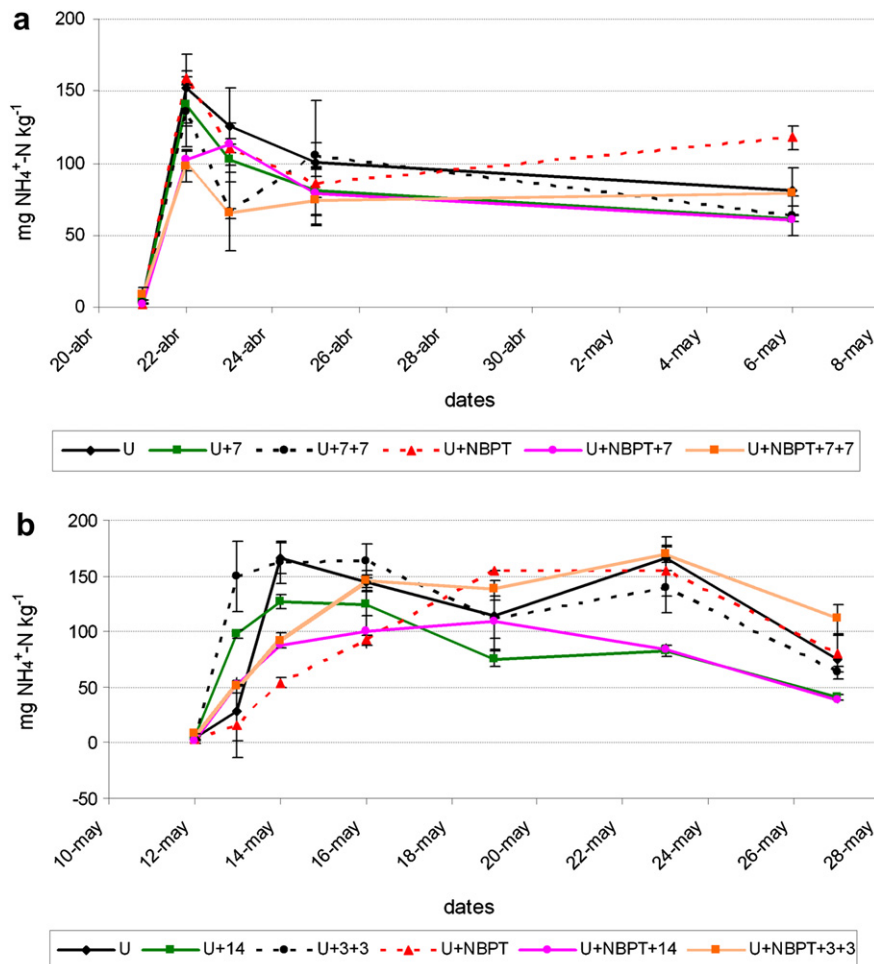

Fig. 2. NH_4^+-N concentrations (mg NH_4^+-N kg^{-1}) in the 0–10 cm soil layer during the Experiment 1 (a) and 2 (b), respectively. Vertical lines indicate standard errors.
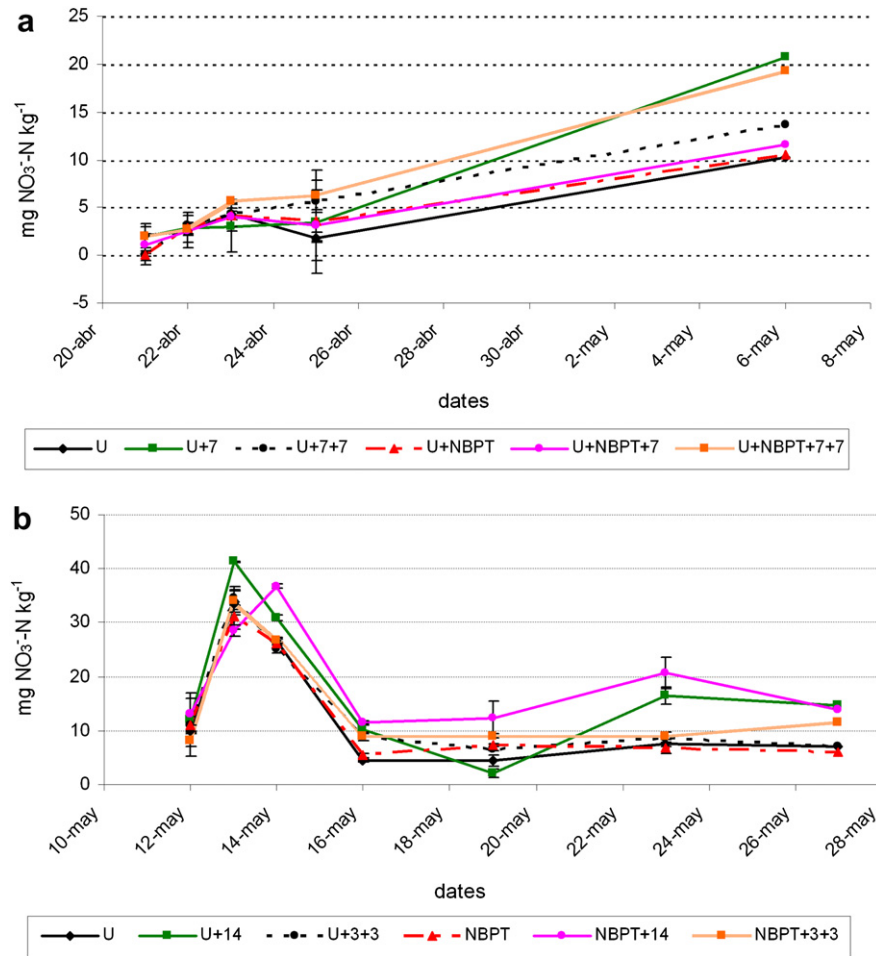
Fig. 3. NO3⁻-N concentrations (mg NO$_3^-$-N kg^{-1}) in the 0—10 cm soil layer during Experiments 1 (a) and 2 (b). Vertical lines indicate standard errors.

between 34.3 and 36.2% with no significant differences between plots. Then, as occurred in experiment 1, the addition of water enhanced soil moisture, reaching values of WFPS up to 49% in the two treatments with 14 mm of irrigation (i.e. U + 14 and U + NBPT + 14). Measured soil temperature was slightly higher than in experiment 1 just after fertilising, at 15 °C, decreasing to 13.2 °C (i.e. 21st May).

3.2.2. Evolution of mineral N and urease activity

There were no significant differences in urease activity between treatments immediately after fertilising. After 24 h, similar to the first experiment, urease activity remained low for the treatments including NBPT. Without NBPT, urease activity increased over the first 24 h. There was no apparent significant effect of irrigation with or without NBPT treatment groupings, with the exception of a greater initial increase in activity from U + 3 + 3 compared with U and U + 14 (Fig. 1b).

An increase in soil NH_4^+ concentration was measured for all treatments 24 h after application, being significantly higher in U (Fig. 2b). Ammonium concentration in U + 14 was significantly lower than that measured in the other two U fertilised soils throughout the experiment. Nevertheless, this concentration was still higher than that of the U + NBPT fertilised plots 48 h after application, after which a progressive increase in NH_4^+ was measured in the U + NBPT fertil-ised plots, with the exception of U + NBPT + 14 soil where values remained below 100 mg NH_4^+-N kg^{-1}. Contrarily, after the initial increase, there was a progressive decrease in the soil NH_4^+ content in

U until the end of the measurement period. An increase in soil NH_4^+ concentration in U + 3 + 3, NBPT and U + NBPT + 3 + 3 was measured 10 days after fertilising (i.e. 23rd of May), coinciding with the second simulated rainfall of 3 mm. Finally, a general decrease in soil NH_4^+ was measured for all treatments from 23rd May until the end of the experiment (Fig. 2b).

The highest concentration of NO_3^- (41.3 mg NO_3^--N kg^{-1}) in the upper soil was twice that of experiment 1, being measured in U + 14 24 h after fertilising. Then, a decrease was measured in all treatments (Fig. 3b), in contrast to the previous experiment where the concentration grown at the end of the measurement period. Soil nitrate concentrations of U + 14 and U + NBPT + 14 were significantly higher than that of other treatments at the end of the sampling period.

3.2.3. Ammonia emission

Ammonia emission rate from U peaked at 7 d after application, some days later than in Experiment 1 (Fig. 4). A similar pattern in emission rate and peak rate value was measured from U + 3 + 3 but with emission rates increasing and peaking 24 h sooner than for U (Fig. 4b).

Irrigation with 14 mm water significantly reduced emission rates, with a peak emission rate after 72 h, much reduced compared with U and U + 3 + 3, after which emission rates were close to zero.

Inclusion of NBPT also significantly reduced emission rates, with rates from U + NBPT and U + NBPT + 14 being close to zero throughout the experiment (Fig. 4b) and those from
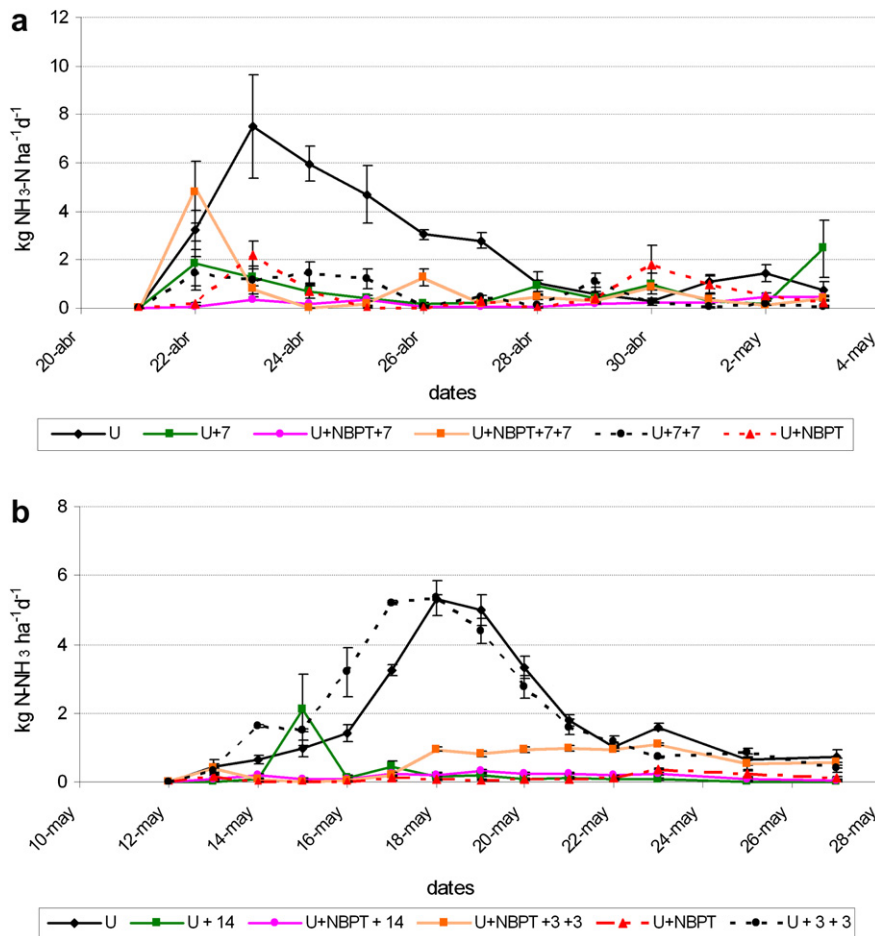
Fig. 4. Ammonia emission rates (kg NH$_3$-N ha^{-1} d^{-1}) after application of urea (U) with or without urease inhibitor (NBPT) in Experiments 1 (a) and 2 (b). Vertical lines indicate standard errors.

U + NBPT + 3 + 3 initially close to zero but increasing to approximately 1 kg NH$_3$-N ha^{-1} d^{-1} for the second week.

Cumulative emissions over 13 d were significantly greater from the U + 3 + 3 and U than other treatments (34.8 ± 0.87 kg N ha^{-1} and 31.8 ± 3.1 kg N ha^{-1}, a 76% and 69% of the N applied respectively), which were not significantly different between them (Table 1).

4. Discussion

4.1. Effect of initial soil moisture and rainfall/irrigation on NH$_3$ emission abatement

Dissolution rate of surface applied urea could have been affected by the initial moisture content of soil. In this study, soil was always wet but the soil moisture prior to the application of treatments differed between the two experiments (averaging 62% and 39% for

Table 1
Cumulative NH$_3$-N fluxes (kg NH$_3$-N ha^{-1}) during the experiment. Data are the averages of means from three replicates ± standard deviation. Different letters within columns indicate significant differences by applying Fish Unprotected Least Significant Difference test at $P < 0.05$.

Experiment 1		Experiment 2	
U	31.4 ± 5.8 d	U	31.8 ± 3.1 c
U + NBPT	7.2 ± 1.5 b	U + NBPT	3.5 ± 1.0 a
U + 7	7.1 ± 2.1 b	U + 14	3.4 ± 1.2 a
U + NBPT + 7	3.2 ± 0.7 a	U + NBPT + 14	3.4 ± 0.3 a
U + 7 + 7	6.8 ± 1.6 b	U + 3 + 3	34.8 ± 0.9 c
U + NBPT + 7 + 7	11.9 ± 0.9 c	U + NBPT + 3 + 3	13.0 ± 2.4 b

experiments 1 and 2, respectively). These different conditions mainly affected the timing of the peak NH$_3$ emission rate, being sooner in the wetter soil (the 2nd and 7th day for experiments 1 and 2, respectively). This may indicate that urea had been more rapidly dissolved in the upper part of the soil under the wettest conditions. Despite this difference, cumulative NH$_3$ emissions from surface applied urea were not significantly different between the two experiments (Fig. 4). Therefore, the differences, in soil moisture and soil temperature, between these two experimental conditions were not a determining factor for NH$_3$ volatilisation, and consequently a robust comparison of the different rainfall patterns evaluated was possible between the two experiments.

Cumulative NH$_3$ emissions measured from the urea-only treatment in the present study were in the range of those reported elsewhere (e.g. Black et al., 1989; Ryden et al., 1987; Sommer and Jensen, 1994; Fox et al., 1996; Van der Weerden and Jarvis, 1997; Sanz-Cobena et al., 2008).

The addition of water (i.e. ≥7 mm) immediately after surface urea application produced a significant reduction in NH$_3$ emissions. This was probably because simulated rainfall, at rates of 7 and 14 mm, would have distributed urea into the soil. Once in the soil, NH$_4^+$ ions, from urea hydrolysis, would have been subsequently immobilised on cation exchange sites, thus reducing the potential for volatilisation. Immediate water addition gave the main effect and there was little subsequent impact on NH$_3$ emission of additional water application 1 week later, presumably because there would have been little urea remaining in the upper soil by this time.

There was little difference in the emission reduction achieved between the 7 mm and 14 mm additions immediately following urea application (77% and 89%, respectively). However, a lower water addition rate (i.e. 3 mm) gave no such abatement in emission, even enhancing them. Water addition would have accelerated urea dissolution and its hydrolysis, which would favour the formation of NH_3 under the conditions of increasing pH associated with urea hydrolysis (Zaman et al., 2009), but the relatively low rate of added water would prevent the urea from being incorporated far into the soil matrix, thus only offering limited protection from volatilisation. This more rapid hydrolysis would explain the earlier increase in emission rate from $U + 3 + 3$ compared with U (Fig. 4b). The results of the present study, although site-specific and influenced by the experimental conditions, would suggest that the UNECE suggested strategy of adding water (i.e. 10 mm) following urea application (UNECE, 2001) is of the correct order, so that while promoting more rapid hydrolysis of the urea it will achieve sufficient incorporation of the dissolved urea into the soil matrix to provide a significant reduction in NH_3 emission.

For drier soils (i.e. WFPS ≤ 20%), it would be expected that a greater amount of water would be necessary in order to achieve an effective mitigation of NH_3 volatilisation. However, the abating effect of adding water after urea fertilising under dry soil conditions may being more effective than for a saturated soil, where the infiltration rate of urea is expected to be low (Singh et al., 1984). This was the interpretation of Sanz-Cobena et al. (2008), who observed that irrigation with 10 mm immediately after urea fertilising of a dry semiarid soil (WFPS ≤ 20%, bulk density of 1.57 g cm^{-3}) resulted in a lower NH_3 emission than expected, according to CORINAIR (2006), had there been no irrigation.

4.2. Effect of NBPT on NH_3 emission

The inclusion of a urease inhibitor, NBPT, with urea application produced a mean reduction in NH_3 emission of 77%, similar to that reported by Dampney et al. (2004) in a tilled soil of the same experimental location (i.e. average reduction 65%). This could be explained by the action of NBPT slowing urea hydrolysis through the inhibition of the urease enzyme in the soil and thus reducing the pool of exchangeable NH_4^+. This allowed more time for urea to diffuse into the soil, lowering the amount of NH_4^+ in the upper soil (0–5 cm) susceptible to be transformed in NH_3 and volatilised (Grant et al., 1996).

However, NBPT was not effective immediately after its application. The inhibitor did not affect urea hydrolysis within the first 24 h after fertilising, probably because an uncompleted oxidation to its active form, NBPTO (Manunza et al., 1999). Because of this, NH_3 emission measured in the non-irrigated U + NBPT treatment was not significantly different to that of the urea-only treatment immediately after fertilising (1st day). A significant effect of the inhibitor on the reduction of NH_3 volatilisation was noticed 24 h after its application. This period was lower than that observed by Sanz-Cobena et al. (2008), who measured an "activation period" of 4 days in a semiarid tilled soil fertilised with urea.

The lower values of urease activity measured in the soil fertilised with U + NBPT at that time (Fig. 1a), and the subsequent low NH_3 volatilisation rates measured, would have been associated with the presence of NBPTO in most of the active sites of the enzyme. However, this effect was only maintained for 3 days.

The slowing effect of NBPT over urea hydrolysis, due to inhibited urease activity, affected the pool of mineral N. Ammonium content of the upper soil (0–10 cm) was lower than in the soil without the inhibitor, immediately after fertilising, followed by declining NH_4^+ concentrations in all treatments. However, the decrease in the pool of NH_4^+, mainly associated to the nitrification process, was lower with the inhibitor than in the soil fertilised with urea alone,

probably due to a progressive loss of inhibition capacity of the inhibitor, which would have been associated with an increase in the urea hydrolysis. Importance of nitrification in the decrease of NH_4^+ would have been confirmed by the high NO_3^- concentration measured 24 h after fertilising in experiment 2 (Fig. 3b). In contrast, the NO_3^- concentration in experiment 1 halved that of experiment 2, probably due to both the urea and N leaching associated to the high soil water content measured.

4.3. Combined effect of water management and NBPT on NH_3 emission

The combined effect on NH_3 emission reduction of using the urease inhibitor NBPT and adding 7 or 14 mm of water to the soil immediately after application was not significantly different to that of the two strategies used separately (c. 80% reduction in both cases). Contrary to our initial hypothesis, that better distribution of NBPT in soil after water addition would enhance the effect, a similar rate of urea hydrolysis was measured for NBPT with water addition than for NBPT alone. This result would indicate that a correct irrigation management may produce a similar abatement effect to that associated with the use of the urease inhibitor NBPT, under the experimental conditions presented here. In contrast, application of an additional 3 mm of water 7 days after the application of U + NBPT increased NH_3 emission rate. This was probably because the second addition of water (i.e. 3 mm) produced a reactivation of urea hydrolysis once the effectiveness of NBPTO ceased, which would have been responsible for the measured increase in the NH_4^+ concentration and in the daily NH_3 emission from the 6th day after fertilising until the end of the experimental period.

A second effect of combining both NBPT and water addition, when fertilising with urea, could be to reduce NH_3 emissions during the so called "activation period". Application of water to the U + NBPT treated soil could have increased NH_3 emission immediately after fertilising by promoting urea hydrolysis at a time when NBPT would not yet have been oxidised to NBPTO. However, the higher irrigation rate applied in the U + NBPT + 7 and the U + NBPT + 14 plots would have incorporated the fertiliser into the soil to such a depth that any NH_3 produced would not have reached the exchange area between soil and air atmosphere (i.e. 0–5 cm depth).

We must be cautious in extrapolating the results from this study, pertaining to the specific soil and micrometereological conditions (e.g. soil pH, temperature and moisture), to other conditions. However, from a qualitative perspective, these results can help to better understand those strategies that could be used in agricultural soils to mitigate NH_3 from urea fertilised soils. Consequently, the use of NBPT by farmers could be limited when irrigation is commonly used. In semiarid countries, where irrigation is a management variable, the careful management of irrigation in relation to urea application could provide both economic and environmental benefits.

Finally, considering the measurement technique used, it is known that the wind tunnel method can bias results when compared to real conditions. Results from the few published studies in which comparisons have been made between measurement techniques, show that wind tunnels commonly give values of emission significantly higher than those estimated with micrometeorological techniques (e.g. Génermont et al., 1998; Loubet et al., 1999a,b; Smith et al., 2000; Misselbrook et al., 2005a,b). However, this methodology is very useful for comparative studies, as in the case of the present study in evaluating different strategies to mitigate NH_3 emission.

5. Conclusions

The addition of water immediately after surface urea application can produce, depending on the rate and frequency of application,

contrasting effects on NH₃ volatilisation. In this study, 3 mm irrigation increased NH₃ emissions by 8%. However, 7 and 14 mm irrigation significantly reduced emissions (by 77 and 89%, respectively), similar to the reduction in emissions achieved through the use of the urease inhibitor NBPT (77%). Combined use of NBPT and water addition did not significantly increase the reduction efficiency. Targeted management of irrigation rate and timing following urea application to crops may therefore represent an alternative NH₃ emission reduction strategy to the use of urease inhibitors in areas where irrigation is common management practice. Although the results of the present study have to be interpreted considering the specific soil conditions under which the experiments were carried out, they provide useful supporting evidence for the suggested UNECE strategy to mitigate NH₃ emissions from urea application through immediate irrigation of 10 mm water.

Acknowledgements

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