Ammonia volatilization losses from surface-applied urea with urease and nitrification inhibitors

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ABSTRACT

Urease inhibitor (UI) and nitrification inhibitor (NI) have the potential to improve N-use efficiency of applied urea and minimize N losses via gaseous emissions of ammonia (NH_3) to the atmosphere and nitrate (NO_3^-) leaching into surface and ground water bodies. There is a growing interest in the formulations of coating chemical fertilizers with both UI and NI. However, limited information is available on the combined use of UI and NI applied with urea fertilizer. Therefore the aim of this study was to investigate the effects of treating urea with both UI and NI to minimize NH_3 volatilization. Two experiments were set up in volatilization chambers under controlled conditions to examine this process. In the first experiment, UR was treated with the urease inhibitor NBPT [N-(n-butyl) thiophosphoric acid triamide] at a rate of 1060 mg kg^{-1} urea and/or with the nitrification inhibitor DCD (dicyandiamide) at rates equivalent to 5 or 10% of the urea N. A randomized experimental design with five treatments and five replicates was used: 1) UR, 2) UR + NBPT, 3) UR + DCD 10%, 4) UR + NBPT + DCD 5%, and 5) UR + NBPT + DCD 10%. The fertilizer treatments were applied to the surface of an acidic Red Latosol soil moistened to 60% of the maximum water retention and placed inside volatilization chambers. Controls chambers were added to allow for NH_3 volatilized from unfertilized soil or contained in the air that swept over the soil surface. The second experiment had an additional treatment with surface-applied DCD. The chambers were glass vessels (1.5 L) fit with air inlet and outlet tubings to allow air to pass over the soil. Ammonia volatilized was swept and carried to a flask containing a boric acid solution to trap the gas and then measured daily by titration with a standardized H_2SO_4 solution. Continuous measurements were recorded for 19 and 23 days for the first and second experiment, respectively. The soil samples were then analyzed for UR−, NH_4^+−, and NO_3^-−N. Losses of NH_3 by volatilization with unamended UR ranged from 28 to 37% of the applied N, with peak of losses observed the third day after fertilization. NBPT delayed the peak of NH_3 losses due to urease inhibition and reduced NH_3 volatilization between 54 and 78% when compared with untreated UR. Up to 10 days after the fertilizer application, NH_3 losses had not been affected by DCD in the UR or the UR + NBPT treatments; thereafter, NH_3 volatilization tended to decrease, but not when DCD was present. As a consequence, the addition of DCD caused a 5−16% increase in NH_3 volatilization losses of the fertilizer N applied as UR from both the UR and the UR + NBPT treatments. Because the effectiveness of NBPT to inhibit soil urease activity was strong only in the first week, it could be concluded that DCD did not affect the action of NBPT but rather, enhanced volatilization losses by maintaining higher soil NH_4^+ concentration and pH for a longer time. Depending on the combination of factors influencing NH_3 volatilization, DCD could even offset the beneficial effect of NBPT in reducing NH_3 volatilization losses.

1. Introduction

Urea (UR) is the N source most widely used in agriculture worldwide (Heffer and Prud'homme, 2011). UR is the primary solid nitrogen fertilizer in the market because of its high N concentration (460 g kg^{-1} N), the restriction against the use of ammonium nitrate, which may be employed as explosives, and the high price of ammonium sulfate. Nitrogen loss through NH_3 volatilization is a primary concern when UR is applied to surfaces of both acidic and alkaline soils because UR is readily hydrolyzed by urease enzymes, causing higher soil pH around the fertilizer granules (Chien et al., 2009; Ernst and Massey, 1960). The amounts of NH_3 lost depend on the type, pH, buffering capacity, temperature and moisture

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content of the soil and can be increased by the presence of plant residues that enhance urease activity in soils (Hargrove, 1988; Terman, 1979). Average NH_3 losses worldwide are of the order of 14% (10–19%) of the N fertilizers used (Ferm, 1998) and are higher in warm climates (Bouwman et al., 2002). For example, several field studies in Brazil reported average losses of 20–30% of the applied N (Cantarella et al., 2003, 2008; Trivelin et al., 2002), but these losses can be as high as 60% (Lara Cabezas et al., 1997).

Besides the economic significance for the farmers, NH_3 losses may have negative ecological impact on atmospheric quality (Zaman et al., 2008, 2009; Zaman and Blennerhassett, 2010; EPA, 2011) and upon returning to the ground cause soil acidification (van der Eerden et al., 1998), act as a secondary source of N_2O production, promote eutrophication of surface water bodies and affect terrestrial biodiversity, especially in sensitive habitats (Sutton et al., 2008; EPA, 2011).

Several products have been studied to minimize the loss of NH_3, including urease inhibitors (Chien et al., 2009). Many organic and inorganic compounds have been tested as urease inhibitors (Kiss and Simihǎian, 2002; Radel et al., 1988), but the best results have been obtained with the urea analogues, particularly N-(n-butyl) thiophosphate triamide (NBPT) (Watson, 2000), which strongly blocks three active sites of the urease molecule (Manunza et al., 1999). NBPT has been tested in several countries with generally satisfactory results at low concentrations (Cantarella et al., 2008; Keerthisinghe and Blakeley, 1995; Rawluk et al., 2001; Watson et al., 1994).

In general, UR hydrolyzes quickly in the soil environment, such that the majority of NH_3 losses occur in the first week after application. The most effective period of urease inhibition by NBPT is relatively short once the fertilizer is applied to the soil (up to 14 days [Trenkel, 2010; Watson, 2000] or even less [Cantarella et al., 2008]). Urea may be incorporated into the soil during this period through mechanical or water (rain or irrigation) means or move down the soil through diffusion thus eliminating or reducing NH_3 volatilization losses (Christianson et al., 1993; Grant et al., 1996; Watson, 2000; Rawluk et al., 2001; Dawar et al., 2011).

The interaction between urease and nitrification inhibitors is also of interest. Nitrification inhibitors are designed to slow the formation of NO_3^- in the soil by inhibiting the oxidation of NH_4^+ to NO_2^- by bacteria of the genus Nitrosomonas (Subbarao et al., 2006). The combination of both inhibitors can potentially result in the reduction of NH_3 volatilization and NO_3^- leaching losses, which may have economic and environmental impacts. Several compounds have been tested as nitrification inhibitors, but the most commercially successful are nitrapyrin, dicyandiamide (DCD) and 3,4-dimethylpyrazole phosphate (DMPP) (Slagen and Kerkhoff, 1984; Trenkel, 2010).

Dicyandiamide is employed in several commercial formulations because it is relatively inexpensive, non-volatile, water-soluble and efficient for use with nitrogen fertilizers at rates of 5–10% of applied nitrogen (Trenkel, 2010). Urea treated with a mixture of DCD and NBPT has been found to have lower N losses by NH_3 volatilization, NO_3^- leaching and N_2O emission (Zaman et al., 2008), which may help to increase N-use efficiency and crop yields (Nastri et al., 2000; Zaman et al., 2008, 2009). However, Prakasa Rao and Puttanna (1987) and

Asing et al. (2008) observed that the addition of DCD to UR caused an increase in NH_3 losses compared with those of UR without the nitrification inhibitor. DCD also caused an increase in NH_3 losses when mixed with urine from animals, which has about 70% of N as urea (Zaman et al., 2009; Zaman and Blennerhassett, 2010).

The addition of DCD can also increase NH_3 losses of NBPT-treated urea and thus reduce the benefits of the urease inhibitor (Gioacchini et al., 2002; Nastri et al., 2000; Zaman et al., 2008). The effects of DCD on NH_3 volatilization are not always consistent. For example, Clay et al. (1990), Blaise et al. (1997) and Banerjee et al. (2002) observed no change in NH_3 losses due to the addition of DCD to urea.

There is interest in combining nitrification and urease inhibitors to allow a reduction of N losses and increase N-use efficiency. Thus, it is important to clarify the effect of DCD on NH_3 volatilization when associated with urease inhibitors as well as to elucidate the possible mechanisms involved in the interaction between these inhibitors. The objective of this study was to evaluate the effect of the combination of DCD and NBPT on NH_3 losses from urea applied to the surface of a soil representative of large agricultural areas in Brazil, where urea is widely applied.

2. Materials and methods

2.1. Characterization of the soil sample

The soil for this study was collected from the 0–20 cm surface layer of a cultivated soil, classified as Typic Hapludox or Red Latosol (Embrapa, 2006). After collection, the sample was air-dried, passed through a 2-mm sieve and analyzed to determine its chemical and physical properties (Table 1). Soil analyses were conducted according to the methods described by Raij et al. (2001) and Camargo et al. (1986); urease activity was determined according to Tabatabai (1982).

2.2. Experiment 1

This experiment was conducted in volatilization chambers under controlled laboratory conditions at the Agronomic Institute in Campinas, Brazil; the temperature was maintained at 25 ± 3 °C, close to the average temperatures of the summer in the State of São Paulo (CIIAGRO, 2012). The fertilizer formulations tested were prilled urea (UR, 1–2 mm in diameter, 456 g kg^{-1} N) with or without the addition of the urease inhibitor NBPT and the nitrification inhibitor DCD. The experiment consisted of five treatments: 1) UR, 2) UR + NBPT, 3) UR + DCD 10%, 4) UR + NBPT + DCD 5%, and 5) UR + NBPT + DCD 10%, with five replicates in a completely randomized design. Unfertilized soil controls and empty chamber controls were included to account for any traces of NH_3 in the air flowing through the system. This resulted in a total of 27 experimental units, arranged randomly.

The fertilizers were weighed on an analytical balance and applied to the surface of the soil at a rate of 203 ± 1 mg N per chamber, which was equivalent to 300 kg N ha^{-1} on a surface-area basis. Such rate expresses the high soil concentration of fertilizer N expected when 80–100 kg ha^{-1} N are band-applied.

Table 1
Chemical and physical properties of the soil samples used.[a]

pH	OM (g dm^{-3})	P (mg dm^{-3})	K (mmol$_c$ dm^{-3})	Ca (mmol$_c$ dm^{-3})	Mg (mmol$_c$ dm^{-3})	H + Al (mmol$_c$ dm^{-3})	CEC (mmol$_c$ dm^{-3})	V (%)	Clay (g kg^{-1})	Silt (g kg^{-1})	Sand (g kg^{-1})	UA (mg N kg^{-1} h^{-1})
5.9	24	219	7.6	47	16	22	93	76	403	94	503	24

[a] pH $CaCl_2$: $CaCl_2$ 0,0125 mol L^{-1}; OM: organic matter: oxi-reduction; P, K, Ca, Mg: extracted with ion-exchange resin; H + Al: buffer solution at pH 7.0; CEC: cation-exchange capacity; V: base saturation; soil texture: densimeter method. UA: urease activity: acetyl monoxime method.