AMMONIA VOLATILISATION FROM UREASE INHIBITOR-TREATED UREA APPLIED TO SUGARCANE TRASH BLANKETS

Heitor Cantarella[1]*; Paulo Cesar Ocheuze Trivelin[2]; Teodoro Leonardo Michelucci Contin[3]; Fábio Luis Ferreira Dias[4]; Raffaella Rossetto[5]; Rafael Marcelino[3]; Renato Badran Coimbra[3,6]; José Antonio Quaggio[1]

[1]*IAC, Centro de Solos e Recursos Ambientais, C.P. 28 - 13001-970 - Campinas, SP - Brasil.*
[2]*USP/CENA, C.P. 96 - 13400-970 - Piracicaba, SP - Brasil.*
[3]*IAC, Programa de Pós-Graduação em Agricultura Tropical.*
[4]*IAC, Centro de Cana, C.P. 206 - 14001-970 - Ribeirão Preto, SP - Brasil.*
[5]*APTA Regional Centro Sul, Caixa Postal 28 - 13400-970 - Piracicaba, SP - Brasil.*
[6]*Usina São João, C.P. 13 - 13600-970 - Araras, SP - Brasil.*
**Corresponding author <cantarella@iac.sp.gov.br>*

ABSTRACT: Legal restrictions from burning sugarcane prior to harvest are causing a sharp increase in acreage which is harvested as green cane. The presence of a thick sugarcane trash mulch left after harvest makes it difficult to incorporate fertilisers in the soil. Since large losses of ammonia may occur when urea is surface applied to trash, it is important to find ways to improve urea-N use efficiency. The urease inhibitor NBPT slows down urea hydrolysis and thus may help decrease ammonia losses. Ammonia traps were set up in seven sugarcane fields covered with trash and fertilised with ammonium sulfate or ammonium nitrate, urea, and NBPT-treated urea. All N fertilisers were surface-applied at rates of 80 or 100 kg N ha^{-1}. Very little N was lost when ammonium nitrate or ammonium sulfate were used. However, volatilisation losses as ammonia from the urea treatments varied from 1% (rainy days after fertilisation) to 25% of the applied N. The percentage of reduction in volatilisation due to NBPT application ranged from 15% to 78% depending on the weather conditions during the days following application of N. Addition of NBPT to urea helped to control ammonia losses, but the inhibitor was less effective when rain sufficient to incorporate urea into the soil occurred only 10 to 15 days or latter after fertiliser application.
Key words: NBPT, nitrogen fertilizer, ammonia losses

VOLATILIZAÇÃO DE AMÔNIA A PARTIR DE URÉIA TRATADA COM INIBIDOR DE UREASE APLICADA SOBRE PALHA DE CANA-DE-AÇÚCAR

RESUMO: Restrições legais à colheita de cana-de-açúcar com despalha a fogo estão causando um aumento da área cultivada com cana crua. Essa prática gera uma espessa camada de palha de cana sobre o solo após a colheita, o que dificulta a incorporação de fertilizantes. Uma vez que grandes quantidades de amônia podem ser perdidas quando a uréia é aplicada superficialmente sobre a palha, é importante buscar alternativas para maximizar a eficiência de uso do N-uréia. O inibidor de urease NBPT retarda a hidrólise da uréia e pode contribuir para diminuir as perdas de amônia por volatilização. Para quantificar essas perdas, foram instaladas câmaras coletoras de amônia em sete áreas de produção de cana-de-açúcar colhida sem queima; estas foram fertilizadas com sulfato ou nitrato de amônio, uréia ou uréia tratada com NBPT. Todos os fertilizantes nitrogenados foram aplicados superficialmente em doses de 80 ou 100 kg ha^{-1}de N. As perdas de N foram muito pequenas quando se usou nitrato ou sulfato de amônio. Entretanto, as perdas por volatilização de amônia decorrentes do uso de uréia variaram de 1% (com dias chuvosos após a adubação) a 25% do N aplicado. O uso de NBPT proporcionou reduções de 15 a 78% nas perdas por volatilização, dependendo das condições climáticas nos dias posteriores à aplicação de N. A adição de NBPT à uréia ajudou a controlar as perdas de amônia, mas o inibidor foi menos efetivo quando chuvas suficientes para incorporar a uréia no solo ocorreram somente 10 a 15 dias, ou mais, após a aplicação dos fertilizantes.
Palavras-chave: NBPT, adubos nitrogenados, perdas de amônia

INTRODUCTION

Urea accounts for about 60% of the N fertilisers used in the Brazilian agriculture. Other important N sources are ammonium nitrate (AN) and ammonium sulfate (AS). However, in view of the relatively high cost per unit of N in AS and the transport restrictions imposed on AN as a result of the likely use of the latter in the manufacture of explosives, urea (UR) is becoming an increasingly important source of N to sugarcane in Brazil. The main restriction in the use of UR is the possibility of high ammonia volatilisation losses when surface-applied to soils (Terman, 1979), whereas this risk is negligible with AS and AN in the predominantly acid soils of Brazil.

Fertiliser incorporation is a common practice in burnt sugarcane, a condition in which UR is usually as efficient as other N sources not subjected to NH_3 losses (Freney et al., 1992; Cantarella et al., 1999). However, recent Brazilian laws requires sugarcane growers to stop burning. In several important growing areas, more than 60% of the fields are harvested and managed without burning. Surface application of urea to soil covered with sugarcane plant residues may cause NH_3 volatilisation losses between 20 and 40% or more of the N applied (Prammanee et al., 1989; Denmead et al., 1990; Cantarella et al., 1999), but fertiliser incorporation in soil under trash is a difficult and expensive operation. Thus, there is an increasing interest in evaluating the efficiency of surface-applied N fertilisers.

One of the possibilities to control or decrease NH_3 losses is to inhibit the rate of urea hydrolysis in the soil. NBPT [N-(n-butyl) thiophosphoric acid triamide] is now the most promising urease inhibitor and has been commercialised in the USA since 1996. NBPT may inhibit urea hydrolysis for periods between 3 and 14 days depending on soil temperature and other environmental conditions, and has been tested in various countries with generally satisfactory results (Watson et al., 1994; Keerthisinghe & Blakeley, 1995; Cantarella et al., 2005). However it is not known if NBPT can be effective when used in fertilisers applied during the dry winter season (June to September) when part of the ratoon sugarcane fertilisation is done in Southwest Brazil (from May to December).

The objectives of this study were to quantify NH_3 volatilisation losses from surface applied urea and to evaluate the effectiveness of NBPT-treated urea when surface-applied to sugarcane soils covered with trash.

MATERIAL AND METHODS

Seven field experiments were carried out from 2002 to 2006 in different regions of State of São Paulo, Brazil: Araras - two experiments (22°21' S; 47°27' W), Iracemápolis (22°34' S; 47°31' W), Araraquara (21°47' S 48°10' W); Pirassununga (21°59' S; 47°25' W), Jaboticabal (21°15' S; 48°19' W), and Ribeirão Preto (21°10' S; 47°48' W). Soil pH ranged between 4.5 and 5.8. The treatments, with four replications in a randomised block design, consisted of the surface application of: (i) urea; (ii) NBPT-treated urea; (iii) a N source not subject to NH_3 volatilisation losses (either ammonium sulfate or ammonium nitrate); and (iv) a control without N. All experiments were set up in sugarcane fields previously harvested without burning and were fertilised to provide N at the rate of either 80 (2002 and 2003 experiments) or 100 kg ha^{-1} N (2004-2006 experiments), amounts commonly used in most sugarcane areas in São Paulo.

Semi-open chambers to trap NH_3 were used to measure the gaseous N loss from fertilisers, following the model described by Nömmik (1973) and modified by Cantarella et al. (2003). The chambers consisted of PVC hollow cylinders, 20 cm in diameter and 40 cm in height, containing two polyethylene foam discs, impregnated with H_3PO_4 + glycerol solution in order to absorb the NH_3 released from the soil. The disc placed in the top position was used to trap potential contamination of the atmospheric NH_3. The lower position disc trapped the NH_3 volatilised from the soil and was used to measure the losses. The upper end of the cylinder was covered with a plastic cap to allow for air circulations.

The PVC chambers were fitted on top of PVC bases, which were cylinders 19 cm in diameter and 20 cm in height and were partially inserted into the soil, leaving around 15 cm of their length above ground. Sugarcane residues were cut with a sharp knife around the bases so that the trash remained inside. Each experimental plot consisted of one chamber and ten bases. The fertiliser treatments were weighed and placed on top of the trash within the PVC bases. The polyethylene foams were replaced periodically, at 2-day intervals in the first two weeks and 3 to 4-day intervals afterwards. Since the chambers do not allow rain or wind to reach the fertiliser placed inside them, and in order to minimise the microclimate effect within the chamber, always when the foams were replaced the chambers were moved to the adjacent PVC base in the same plot. Thus, the NH_3 loss assessment of the following period was done with a fertiliser treatment that had been exposed to the same conditions (rain, temperature, wind etc) as the remaining field. The chambers were also moved to the next base after any raining event along the sampling interval.

NBPT was added to urea about two days before its use in the field. The rate of application was 1,325 mg NBPT per kilogram urea in the trial laid down at Iracemapolis in 2003 whereas, at the other six study sites, 530 mg NBPT per kilogram urea was applied. The urease inhibitor used was in a solution containing 200 g kg^{-1} NBPT in a mixed solvent consisting of N-methyl-2- pyrrolidone and inert ingredients, supplied by Agrotain International, L.L.C (St. Louis, MO, EUA). Discs collected in the field were sealed in plastic bags and stored in a refrigerator at 5°C until analysis. Ammonia trapped by the foam discs at the lower position in the chamber was extracted by leaching, followed by squeezing, with five consecutive portions of 100 mL of 1.0 mol L^{-1} KCl solution. An aliquot of the extract was steam-distilled with 10 mL of 5.0 mol L^{-1} NaOH solution, and then titrated with 0.025 mol L^{-1} H_2SO_4 for NH_4^+-N determination (Bremner, 1965). The results are reported as percentage of the N added to the chamber bases.

RESULTS AND DISCUSSION

In the experiment of Iracemapolis (Figure 1A), a 30 mm rainfall had occurred before the experiment was setup but, when the fertiliser treatments were applied, the trash was almost dry. Temperatures were relatively low (14°C) for this time of the year. Except for small amounts of rain, the weather remained relatively dry for about one month. Volatilisation was dependent on weather conditions. Initially the volatilisation losses were low because of the windy and dry weather in the first days following N application. A 2.6 mm rainfall on the fifth day probably triggered urea hydrolysis and, therefore, NH_3 volatilisation. Other small rainfalls (1.4 mm) 25 and (7.2 mm) 30 days after fertilisation caused an additional slight increase in NH_3 losses but it seems that, at this time, the potential for losses was already small. NBPT-treated urea only started to have volatilisation losses seven days after fertiliser application. Volatilisation proceeded at a slow pace until about the 35th day and then subsided. At the end of the Iracemapolis experiment, losses of NH_3 from AN treated plots were negligible (0.26% of applied N) but attained 25% and 15.2% of the N applied when UR and UR-NBPT were used respectively (Figure 1A). All means were different (Tukey $p \le 0.05$).

In Araras, the weather was dry except for a light rainfall (0.6 mm) on 4th Nov so that the cane mulch was dry when the fertiliser was applied on the 6th Nov. Later in that same day a sudden change of weather, typical of Brazilian spring and summer, took place around the experimental area and a fast but intensive shower (13.8 mm) occurred.

Volatilisation losses measured 20 h after fertiliser application were negligible indicating that little urea hydrolysis took place in that interval. However, on the second day after N application, NH_3 losses with UR reached 2.5% of the N added and peaked in the fourth day (3.5% of N applied). Volatilisation losses with the UR treatment followed the same pattern observed in previous experiments but with a lower intensity, probably due to the rain that occurred after fertiliser application (Figure 1B).

The 13.8 mm rainfall was not sufficient to incorporate most of the UR into the soil but it may have caused a decrease in volatilisation losses. Ten to 20 mm rain or irrigation is considered sufficient to stop or drastically reduce NH_3 volatilisation when urea is surface-applied to bare soil (Terman, 1979; Hargrove,

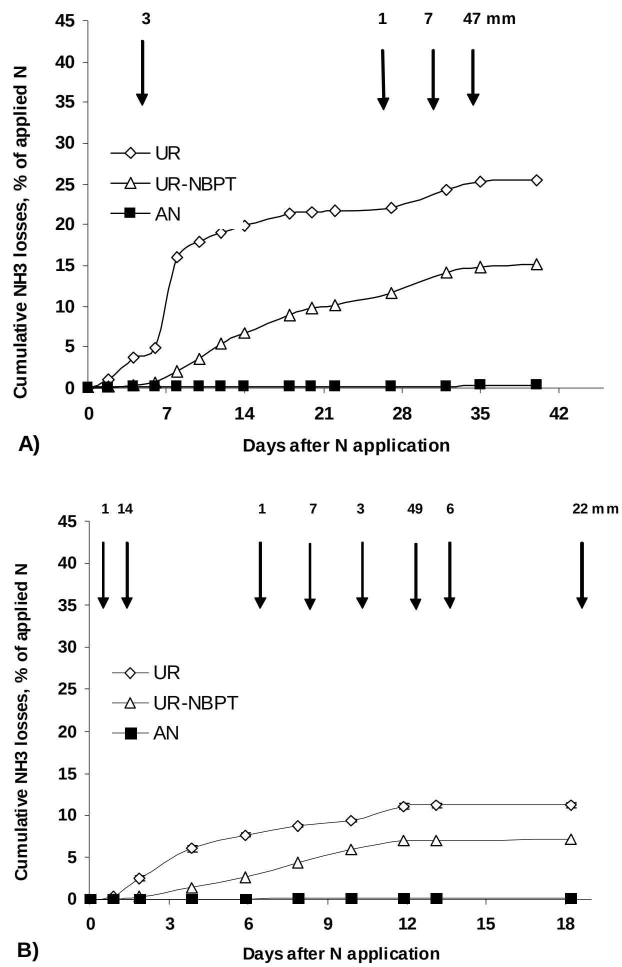

Figure 1 - Cumulative NH_3 losses from urea (UR), NBPT-treated urea (UR-NBPT) and ammonium nitrate (AN) following surface application to a trash-covered sugarcane soil. (A) Iracemapolis and (B) Araras experiments. Figures above arrows indicate the amount (mm) and position of arrows indicate the time of rain events. Experiments started on 25th Sep (end of dry season) in Iracemapolis and on 6th Nov in Araras.

Table 1 - Ammonia losses by volatilisation from seven field experiments comparing ammonium nitrate (AN) or ammonium sulfate (AS) with urea (UR) or NBPT-treated urea surface-applied to sugar field covered with trash.

Location	Month	Prevalent weather condition	NH_3 losses from			reduction by NBPT
			AS or AN	UR	UR-NBPT	
			------------------ % of applied ------------------			%
Araras	Nov	Rainy	0.1	11.2	7.2	36
Iracemapolis	Sep	Dry	0.2	25.4	15.2	40
Araraquara	Oct	Dry	0.2	25.1	21.3	15
Pirassununga	Dec	Rainy	0.1	7.2	1.6	78
Araras II	Aug	Dry	0.4	16.4	13.4	18
Jaboticabal	Nov	Very rainy	0.1	1.1	0.8	-
Ribeirão Preto	Jun	Dry	0.3	15.2	11.2	26

1988). However, because of the presence of trash, a greater amount of rain may be required and, as reported by Haysom et al. (1990), a 10 mm rainfall was found to be insufficient to effectively reduce NH_3 losses when urea was applied to an unburned sugarcane field.

Freney et al. (1991) observed that more than 16 mm rainfall were needed to cause reduction in NH_3 volatilisation whereas Calcino & Burgess (1995) concluded that 23 mm were not sufficient to dissolve all the urea and incorporate it into the soil. In Brazil, Oliveira et al. (1999) observed that there were still some NH_3 losses after 38 mm of rain. The higher amounts of water needed to incorporate UR in trash-covered soil could be because the water may flow through preferential channels formed within the plant residue cover so that the rain does not efficiently dissolve and leach the urea into the underneath soil (Freney et al., 1994)

In Araras, small amounts of rain fell in subsequent days but volatilisation losses only stopped when a 49 mm rainfall occurred on the 12th day (Figure 1B). The cumulative losses of NH_3 reached about 12% of the N applied as UR. For UR-NBPT, volatilisation losses started on the 4th day and continued slowly until the 49 mm rainfall event took place; the gradual hydrolysis caused the rates of loss to be relatively low as opposed to that of untreated urea which tend to have volatilisation concentrated in a short period of time due to the fast break down of the urea molecule. Cumulative losses of NH_3 with UR-NBPT reached 7% of the N applied (Figure 1B). The same pattern was observed in the five other experiments with NH_3 volatilisation and the total amount of N lost being strongly dependent on the climate (Table 1).

As expected, volatilisation losses with AS or AN were very small (Table 1). For UR, NH_3 losses varied from 1.1% of the applied N in a place where heavy rain fell soon after fertiliser application, to about 25% under less favourable conditions. The addition of NBPT caused a reduction in volatilisation losses that varied from 15% to 78%, compared with those of untreated UR. In the case of the higher reduction of N loss (Pirassununga), even the volatilisation observed with the UR treatment was small due to the occurrence of rain soon after fertiliser application so that the 78% N loss reduction was of little practical significance.

CONCLUSIONS

The urease inhibitor indeed has contributed to reduce NH_3 losses but, in the experiments under dry conditions, the effect of NBPT tended to be small because, after the inhibitory effect on urease subsided, the fertiliser still remained unincorporated in the soil and, therefore, still subject to volatilisation losses. Furthermore, the NH_3 losses that occurred under long periods of dry weather during the winter months (Jun to Aug) seem to be relatively low: less than 20% of applied N at most sites. The results obtained indicated that, with AN and AS, there were negligible NH_3 losses and that these fertilisers would be the preferable N sources for surface application in unburned sugarcane. However, the lower cost and availability can make urea a more competitive N source particularly in situations where losses are expected to be low as in very dry and cool months. Depending on cost, NBPT, although only partially effective in reducing NH_3 volatilisation losses, can help to increase UR fertiliser efficiency.

ACKNOWLEDGEMENTS

The authors are grateful do FAPESP and CNPq for financial support and to the Organizing Comittee of the XXVIth Congress of the ISSCT (Durban, South Africa, 29 July to 02 August 2007, where this the paper was present), for allowing the publication of this article.

REFERENCES

BREMNER, J.M. Inorganic forms of nitrogen. In: BLACK, C.A. (Ed.) **Methods of soil analysis.** Part 2. Chemical and microbiological properties. Madison: American Society of Agronomy, 1965. p.1179-1237.

CALCINO, D.V.; BURGESS, D.J.W. Effect of urea placement on crop cycle yields of green trash blanketed sugarcane ratoons. **Proceedings of Australian Society of Sugar Cane Technologists,** v.17, p.193-198, 1995.

CANTARELLA, H.; MATTOS JÚNIOR, D.; QUAGGIO, J.A.; RIGOLIN, A.T. Fruit yield of Valencia sweet orange fertilized with different N sources and the loss of applied N. **Nutrient Cycling in Agroecosystems,** v.67, p.215-223, 2003.

CANTARELLA, H.; QUAGGIO, J.A.; GALLO, P.B.; BOLONHEZI, D.; ROSSETTO, R.; MARTINS, A.L.M.; PAULINO, V.T.; ALCÂNTARA, P.B. Ammonia losses of NBPT-treated urea under Brazilian soil conditions. In**:** INTERNATIONAL FERTILIZER INDUSTRY ASSOCIATION INTERNATIONAL WORKSHOP ON ENHANCED-EFFICIENCY FERTILIZERS, Frankfurt, 2005. **Proceedings**. Paris: International Fertilizer Industry Association, 2005. 1 CD-ROM.

CANTARELLA, H.; ROSSETTO, R.; BARBOSA, W.; PENNA, M.J.; RESENDE, L.C.L. Perdas de N por volatilização da amônia e resposta da cana-de-açúcar à adubação nitrogenada em sistema de colheita de cana sem queima prévia. In: CONGRESSO NACIONAL DA STAB, 7., Londrina, 1999. **Anais**. Piracicaba: STAB, 1999. p.82-87.

DENMEAD, O.T.; FRENEY, J.R.; JACKSON, A.V.; SMITH, J.W.B.; SAFFIGNA, P.G.; WOOD, A.W.; CHAPMAN, L.S. Volatilisation of ammonia from urea and ammonium sulfate applied to sugarcane trash in North Queensland. **Proceedings of Australian Society of Sugar Cane Technologists,** v.12, p.73-78, 1990.

FRENEY, J.R.; DENMEAD, O.T.; SAFFIGNA, P.G.; WOOD, A.W.; CHAPMAN, L.S.; HURNEY, A.P. Ammonia loss from sugar cane fields as affected by fertilizer placement, irrigation and canopy development. **Proceedings of Australian Society of Sugar Cane Technologists,** v.13, p.38-43, 1991.

FRENEY, J.R.; DENMEAD, O.T.; WOOD, A.W.; SAFFIGNA, P.G. Ammonia loss following urea addition to sugar cane trash blankets. **Proceedings of Australian Society of Sugar Cane Technologists,** v.16, p.114-121, 1994.

FRENEY, J.R.; DENMEAD, O.T.; WOOD, A.W.; SAFFIGNA, P.G.; CHAPMAN, L.S.; HAM, G.J.; HURNEY, A.P.; STEWART, R.L. Factors controlling ammonia loss from trash covered sugarcane fields fertilized with urea. **Fertilizer Research,** v.31, p.341-349, 1992.

HARGROVE, W.L. Soil, environmental, and management factors influencing ammonia volatilization under field conditions. In: BOCK, B.R.; KISSEL, D.E. (Ed.) **Ammonia volatilization from urea fertilizers.** Muscle Shoals: Tenessee Valley Authority-National Fertilizer Development Center, 1988. p.17-36. (Bull. Y-206).

HAYSOM, M.B.; CHAPMAN, L.S.; VALLIS, I. Recovery of nitrogen from ^{15}N urea applied to a green cane trash blanket at Mackay. **Proceedings of Australian Society of Sugar Cane Technologists,** v.16, p.79-84, 1990.

KEERTHISINGHE, D.G.; BLAKELEY, R.L. Inhibition of jack bean urease by phosphoric- and thiophosphoric triamides. **Soil Biology and Biochemistry,** v.27, p.739-742, 1995.

NÖMMIK, H. The effect of pellet size on the ammonia loss from urea applied to forest soil. **Plant and Soil,** v.39, p.308-318, 1973.

OLIVEIRA, M.W.; TRIVELIN, P.C.O.; BENDASSOLLI, J.A.; Volatilização de amônia da uréia (^{15}N) aplicada ao solo com e sem cobertura de palhada em diferentes manejos na adubação de soqueira de cana-de-açúcar. In: CONGRESSO NACIONAL DA STAB, 7., Londrina, 1999. **Anais**. Piracicaba: STAB, 1999. p.86-99.

PRAMMANEE, P.; SAFFIGNA, P.G.; WOOD, A.W.; FRENEY, J.R. Loss of nitrogen from urea and ammonium sulphate applied to sugar cane crop residues. **Proceedings of Australian Society of Sugar Cane Technologists,** v.11, p.76-84, 1989.

TERMAN, G.L. Volatilization losses of nitrogen as ammonia from surface-applied fertilizers, organic amendments, and crop residues. **Advances in Agronomy**, v.31, p.189-223, 1979.

WATSON, C.J.; MILLER, H.; POLAND, P.; KILPATRICK, D.J.; ALLEN, M.B.C.; GARRET, M.K.; CHRISTIANSON, C.B. Soil properties and the ability of the urease inhibitor N-(n-butyl) thiophosporic triamide (nBTPT) to reduce ammonia volatilization from surface-applied urea. **Soil Biology and Biochemistry,** v.26, p.1165-1171, 1994.

Received September 05, 2007
Accepted December 14, 2007