Ammonia volatilization, dry matter yield and nitrogen levels of Italian ryegrass fertilized with urea and zeolite

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Abstract
The nitrogen loss by ammonia volatilization is one of the main factors for low efficiency of N-urea applied on the soil surface. The reduction of losses by volatilization can be obtained with the addition of zeolites to the urea fertilizer. Zeolites are hydrated crystalline aluminosilicate minerals of alkaline and alkaline earth metals, structured in rigid third dimension net, organized by AlO_4 and SiO_4 tetrahedral and of natural occurrence. The objective of this study was to evaluate ammonia volatilization, dry matter yield and nitrogen levels of Italian ryegrass fertilized with urea and zeolite. A pot experiment in a randomized blocks design with four replications was carried out. Treatments comprised: urea, urea incorporated in soil, urea-NBT, urea coated with zeolite, ammonium sulfate, ammonium nitrate and control applied at the level of 50 kg/ha of N on soil surface. Ammonia volatilized was captured by a foam absorber with politetrafluoroetilene. Results showed the potential for urea and zeolite to improve the efficiency of nitrogen use, since the use of the mineral provided similar effects to the treatments with lower volatility losses and were inferior only to those sources do not exhibit volatility losses (NH_4SO_4 and NH_4NO_3) and to that of with urease inhibitor (urea-NBT).

Key Words
Stilbite, *Lolium multiflorum* Lam., nitrogen fertilizer, N losses.

Introduction

Urea nitrogen has been the most used N-source in Brazil (Anda 2003), due to lower cost per unit of N. But N use efficiency of urea may be reduced because of losses from agricultural system by volatilization of ammonia to atmosphere. This is one of the main factors responsible for the low efficiency of urea, and may reach extreme values, close to 80% of N applied (Lara Cabezas *et al.* 1997), even so in acid soils, since the liming increases soil pHs and favors volatilization. Mulch form no-tillage or pasture systems may also increase the amount of N lost by volatilization, especially when urea is applied on soil surface.

A reduction of this loss can be reached through the use of sources less susceptible to volatilization (nitric or ammoniac), or by soil incorporation of the urea (a process hindered by direct fertilization). Slow urea liberation have also be observed with the addition of acids, salts of K, Ca and Mg, and by the choice of specific urea's grain size distribution (Allaire and Parent 2004).

The N-urea losses can also be reduced using zeolites as additives in the fertilizers to control the retention and release of NH_4^+. There are reports in the literature showing that the addition of zeolite to the source of N can improve the nitrogen use efficiency (Ming and Mumpton 1989; McGilloway *et al.* 2003; Gruener *et al.* 2003; Rehakova *et al.* 2004). Zeolite minerals are crystalline hydrated aluminosilicates of alkali or alkaline-earth metals, structured in three-dimensional rigid crystalline network, formed by the tetrahedral AlO_4 and SiO_4, which come together to compose a system of canals, cavities and pores (Ming and Mumpton 1989).
These naturally occurring minerals have three main properties, which are of great interest for agricultural purposes: high cation exchange capacity, high water holding capacity in the free channels, and high adsorption capacity. The main action of zeolite in ammonium conservation is a decrease in N concentration in soil solution through cation exchange. Besides retaining large quantities of ammonium ion, these minerals also interfere with the process of nitrification (Bartz and Jones 1983; Fergunson and Pepper 1987). The increased efficiency of N utilization when urea is used together with zeolite was demonstrated by Crespo (1989), Bouzo *et al.* (1994), and He *et al.* (2002) that achieved increasing of N use efficiency, N uptake and dry matter yield and reductions of losses by ammonia volatilization.
While zeolites are useful for increasing N use efficiency in a range of crops, no information exists on the

degree to which they might decrease ammonia emission and enhance N use efficiency in agricultural systems where urea-N is used, especially on acid soils. The objective of this study was to evaluate ammonia volatilization, dry matter yield and nitrogen levels of Italian ryegrass fertilized with urea and zeolite.

Methods

The green house experiment was conducted at Embrapa Pecuária Sudeste, in Sao Carlos (22°01' S and 47°54' W; 856 m above sea level), State of Sao Paulo, Brazil. Italian ryegrass (*Lolium multiflorum* Lam) was grown in pots with 3 kg completed with soil samples taken at a 0-0.2 m deep layer from Typic Hapludox. Soil presented the following chemical properties: $pHCaCl_2$ = 6.3, organic matter = 25 g/dm^3, P_{resine} = 15 mg/dm^3, K = 1.8 mmol$_c$/dm^3, Ca = 23 mmol$_c$/dm^3, Mg = 13 mmol$_c$/dm^3, CEC = 59 mmol$_c$/dm^3, and basis saturation = 64%; and the physical characteristics: 541 g/kg of sand, 74 g/kg of silt and 385 g/kg of clay. Pots were uniformly limed (until V = 70%) before planting and fertilized at planting with 200 mg/kg of P_2O_5, 100 mg/kg of K_2O and 1.8 mg/kg of Zn.

Zeolite used was collected in the North of State of Tocantins, Brazil, in the basin of the Parnaiba river (Rezende and Angelica 1999). It had 470 g/kg of stilbite. The material was crushed and part of it was concentrated, separating contaminants (quartz and iron oxides and hydroxides) from zeolite by means of gravitational concentration, using the Humphrey spiral, resulting in material with 650 g/kg stilbite and particle size of <1 mm (16 mesh).

The experiment was arranged in a randomized block design with four replications. Treatments comprised: a) urea applied in soil surface; b) urea incorporated in soil at 0.05 m depth; c) urea-NBT (urease inhibitor); d) urea mixed with 200 g/kg of zeolite and applied in soil surface; e) ammonium sulfate; f) ammonium nitrate and g) control (without N). Treatments were applied at the level of 50 kg/ha of N after first shoot cut with the topdressing fertilization.

The collectors for volatized ammonia capture (Campana *et al.* 2009) were composed of a foam of 0.08.x 0.08 m size with 20 kg/m^3 density and soaked with 11 ml of phosphoric acid solution (0.5 N) placed 0.05 m over soil surface. Subsequently, the foams were placed over PVC plates (0.1 x 0.1 x 0.002 m) and wrapped with one layer of polytetrafluoroethylene tape (PTFE) up, which is permeable by ammonia and impermeable by the water. The foam and absorbers from the collectors were changed every two days to determine the volatilized ammonia, performing 11 samples taken in a period of 22 days.

Italian ryegrass shoot was sampled at the beginning of flowering. Total concentration of N in shoot samples was determined after hot sulfuric digestion by a standard micro-Kjeldahl system (Nogueira and Souza 2005).

Nitrogen use efficiency (NUE), agronomic efficiency (AE), crop recovery efficiency (RE) and physiological efficiency (PE) of applied urea-N with zeolite were computed using the following formulae, as suggested by Dobermann (2007):

$NUE = Y_N/F_N$ (g of harvest product per g of N applied),
$AE = (Y_N - Y_0)/F_N$ (g of yield increase per g of N applied),
$RE = (U_N - U_0)/F_N$ (g of increase in N uptake per g of N applied),
$PE = (Y_N - Y_0)/(U_N - U_0)$ (g of yield increase per g of increase in N uptake from fertilizer),

Wherein,
F_N = amount of (fertilizer) N applied;
Y_N = crop yield with applied N;
Y_0 = crop yield in a control treatment with no N;
U_N = total plant N uptake in aboveground biomass in a plot that received N;
U_0 = total N uptake in aboveground biomass in a plot that received no N.
Data of ammonia volatization, dry matter yield and nitrogen shoot concentrations were tested for differences among treatments using a complete randomized block analysis of variance. The Duncan test was used for determining differences between means.

Results

The estimative of volatilized NH_3-N loss by the foam absorber in each treatment over the 22 days of sampling period is shown in Figure 1. Results showed that the maximum loss of NH_3-N is concentrated from the fourth to the tenth day after the urea application. During this period the losses are considered more relevant this results are in agreement with those obtained by Campana *et al.* (2009) using the same methodology. Exception was the urea with urease inhibitor (NBT), which maximum occurred at the fifth day until eighteenth day after supply. The smallest losses by volatilization occurred with ammonium sulphate and ammonium nitrate and control.

The best dry matter yield and N uptake (Table 1) was obtained with the nitrogen sources ammonium sulphate and ammonium nitrate. The yields obtained with urea coated with zeolite (200g/kg) were statistically equivalent to both urea-NBT and urea incorporated to 0.05 m. N uptake in aboveground biomass followed the same trend.

Maximum N content in shoot observed was 19.4 g/kg achieved with urea incorporated in soil at 5 cm depth (Table 1), followed by ammonium sulphate and ammonium nitrate treatments. Nitrogen content from urea with zeolite treatment wasn't statically different of urea with urease inhibitor and urea applied to soil surface. Nevertheless, these values were 4, 35, 29 and 9% higher than those of the control. The principle of foliar diagnosis is based on comparing nutrient concentrations in leaves with standard values. Crops are considered to integrate factors such as presence and availability of soil mineral N, weather variables, and crop management. Leaves are associated with metabolic activity, such as photosynthesis and high nitrogen. The range of levels considered adequate for N in Italian ryegrass shoot range 23 and 27 g/kg (Hopkins *et al.* 1995). Thus, the values obtained were considered low even so the best treatment.

Nitrogen use efficiency is also called the partial factor of productivity of applied N, which is an aggregate efficiency index that includes contributions to crop yield derived from uptake of indigenous soil N, N fertilizer uptake efficiency, and efficiency of conversion of N acquired by plants to DM yield. Agronomic efficiency is the product of the N recovery from applied N sources, physiological efficiency is the efficiency with which the plant uses each unit of N acquired from applied N to produce biomass and crop recovery efficiency represents the degree of congruence between plant N demand and available supply of N from applied fertilizer (Dobermann 2007). Results showed that there were statistical differences between treatments in NUE, AE, PE and RE (Table 1). The lower ratio of DM yield to the amount of applied N (NUE) and AE was observed with urea applied on soil surface and the highest was obtained with ammonium sulfate. Urea coated with zeolite showed intermediate values. Physiological efficiency and RE were more sensitive variables to evaluate the variations in N fertilizer sources treatments.

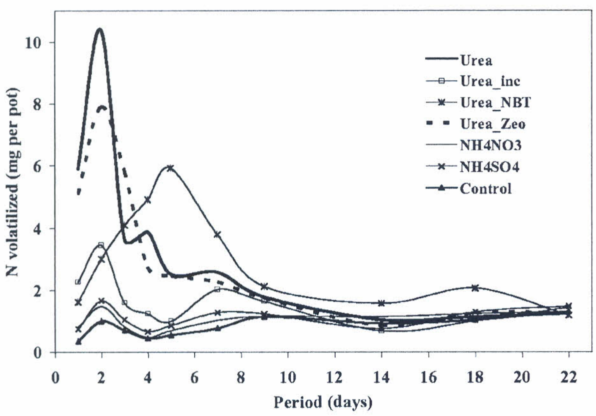

Figure 1. Daily rate of volatilization of ammonia (mg per pot) according to N sources.

Table 1. Ammonia volatilization and Italian ryegrass dry matter yield, N shoot content, N uptake in aboveground biomass, nitrogen use efficiency (NUE), agronomic efficiency (AE), crop recovery efficiency (RE) and physiological efficiency (PE) according to N sources.

Treatment	*Ammonia volatilization*		*Dry matter*	*N content*	*N uptake*	*NUE*	*AE*	*RE*	*PE*
	(mg per pot)	(% total)	(g per pot)	(g/kg)	(g per pot)			(g/g)	
Urea	36.19 A	21.17 A	5.38 B	13.9 C	74.9 D	31.4 B	26.0 B	365.8 D	20.6 A
Urea-soil incorporated	18.14 B	10.61 B	5.88 AB	19.4 A	113.0 AB	34.4AB	28.9 AB	588.8 AB	14.1 C
Urea-NBT	32.43 A	18.86 A	6.33 AB	15.4 C	97.1 BC	37.0 AB	31.6 AB	495.9 BC	15.7 BC
Urea with zeolite	33.43 A	19.55 A	5.58 B	14.6 C	81.33 DC	32.6 B	27.2 AB	403.6 CD	14.9 C
Ammonium sulphate	12.71 B	7.43 B	6.75 A	17.9 AB	120.5 A	39.5 A	34.0 A	632.5 A	18.7 A
Ammonium nitrate	11.69 B	6.83 B	6.30 AB	17.3 B	109.7 AB	36.8 AB	31.4 AB	569.3 AB	18.0 AB
Control	9.78 B	-	0.93 C	13.4 C	12.3 E	-	-	-	-

Values followed by different letters are significantly different according to Duncan test ($p<0.05$) among N sources.

These results indicate that zeolite minerals are able to contribute to increasing N uptake through the control of retention of ammonium ion – formed by urea hydrolysis in the soil, due to zeolite high cation exchange capacity and ammonium withdrawal from soil solution (Bartz and Jones 1983; Ferguson and Pepper 1987). Results agree with those obtained by Crespo (1989), Bouzo *et al.* (1994), and He *et al.* (2002), who also found beneficial effects when using this mineral together with urea.

Conclusion

Results showed the potential for urea and zeolite to improve the efficiency of nitrogen use, since the use of the mineral provided similar effects to the treatments with lower volatility losses and were inferior only to those sources do not exhibit volatility losses (NH_4SO_4 and NH_4NO_3) and to that of with urease inhibitor (urea-NBT).

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