



Ammonia volatilization and availability of Cu, Zn induced by applications of urea with and without coating in soils

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Abstract

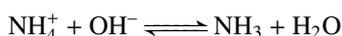
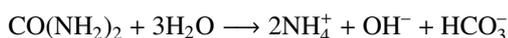
Ammonia volatilization and the distribution of Cu and Zn were investigated in two types of soil treated with coated and uncoated urea. The rate of ammonia volatilization in two weeks after fertilizing with coated urea was 8% in soil 1 (soil derived from river alluvial deposits in Dongting Lake Plain) and 5.15% in soil 2 (red soil derived from quaternary red clay), about half the rates observed when fertilizing with common urea, implying that the hydrolysis speed of the coated urea was lower than for common urea, and that the coated urea can increase nitrogen use efficacy. As for the availability of Cu and Zn, their concentrations decreased in the first week after fertilization, and then increased, which was contrary to the effect of treatment on soil pH. For example, when the pH was 7.99, there was 0.79 mg/kg exchangeable Cu and 0.85 mg/kg exchangeable Zn in the soil derived from river alluvial deposits in Dongting Lake Plain. However, the concentrations of exchangeable Cu and Zn were generally lower for the common urea treatments than those with the coated urea because the peak pH for the common urea treatment was greater. The concentrations of these elements correlated well with pH in the range 4–8 in second order polynomial fits.

Key words: ammonia volatilization; coated urea; soil; metal element

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Introduction

China is the largest consumer of chemical fertilizers in the world and the second largest producer (Wang et al., 1996). The fertilizer application rate has increased over the years, from 58.9 kg/ha in 1978 to 332.8 kg/ha in 2007 (Han et al., 2009). The excess amount of N fertilizers has directly affected the productivity in some areas by reducing the soil fertility (Rozelle et al., 1997). Urea is the most common fertilizer used in Chinese agriculture. It plays an essential role in plant production compared to other nitrogenous fertilizers. The increasing importance of urea as a fertilizer can be attributed to its high nitrogen content, low cost and convenient use. However urea has inherent disadvantages due to its low nitrogen use efficiency. It has been estimated that loss of fertilizer N ranges from 20% to 80% of the urea (Hargrove and Kissel, 1979). Urea can be easily hydrolyzed by the enzyme urease via the following processes:



Ammonia volatilization is a major channel for N loss from the surface after application of urea (Fenn and Miyamoto, 1981), accounting for a loss ranging from 1% to 60% of the applied N on agricultural soils (Volk, 1959; Matocha, 1976; Christianson, 1989). Therefore, urea application can result in a significant economic loss and severe environmental pollution. However, controlled-release fertilizers have been shown to reduce N loss, thereby increasing fertilizer efficiency and potentially decreasing its contribution to environmental pollution (Martin, 1997). To date, controlled-release fertilizers have been studied intensively worldwide. Whereas research has focused on the development and nitrogen usage efficiency of new controlled-release fertilizers, the environmental impacts have been neglected so far (Shoji and Kanno, 1994; Shaviv and Mikkelsen, 1993).

Micronutrient malnutrition is a growing concern in the developing countries, resulting in diverse health and social problems, such as mental retardation, impairment of the immune system and overall poor health. In most cases, the reason is inadequate dietary intake of micronutrients (Welch and Graham, 2004). Tang et al. (2008) found that 43 cultivars had low Fe (average 28.2 mg/kg) and Zn (28.6 mg/kg) concentrations in crop grain in Shandong (China).

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Analysis of nearly 250,000 soil samples and 25,000 plant samples collected from different states in India showed that 48% of the soil samples and 44% of the plant samples contained inadequate levels of Zn (Singh, 2007). The percentages of the soil samples deficient in Fe, Cu and Mn were 11%, 7% and 5%, respectively (Singh, 1998). It is known that following urea hydrolysis, hydrogen ions are consumed and soil pH increases. On the contrary, hydrogen ions are produced and consequently soil pH decreases during the follow-up process of nitrification. The variation of soil pH may cause changes in the bioavailability of soil elements. However, the information on the quantitative relationships between soil pH and content of exchangeable elements during short-term fertilizer application is limited. Moreover, in the literature the environmental effects of N losses have only focused on agricultural soils, while studies on horticultural soils are very sparse (He et al., 2005). Therefore, in this incubation experiment, we studied the ammonia volatilization from common urea and coated urea application in two different types of soils, and how urea application affected the bioavailability of two metal elements: Cu and Zn. The objectives of this study were to assess the difference between common urea and coated urea in nitrogen use efficiency in horticultural soils from South China to: (1) determine the effect on the relationship between pH and exchangeable metal element concentrations after urea application in the soil samples; and (2) analyze the time-dependent dynamics of pH and exchangeable metal element concentrations in soils.

1 Materials and methods

1.1 Soils and fertilizers

Two different soils were used in this study. One was the soil derived from river alluvial deposits in Dongting Lake Plain (soil 1), and the other one was red soil derived from quaternary red clay (soil 2). They were collected from a plot of vegetable garden soil in Hunan Province (28.2°N 113.1°E), southern China. These samples were taken from the surface layer (0–20 cm) of cultivated soils in which vegetables had been grown. The samples were air-dried, and then passed through a 2-mm sieve, homogenized and stored in plastic containers until use. The physical and chemical properties of the soils tested are listed in Table 1. Fertilizers used were common urea (46.0% N content, produced by Jiangfeng Chemical Factory, China) and coated urea (25.5% N content, produced by South China Agricultural University, China).

1.2 Soil treatments

The air-dried soil samples of 100 g (soil 1 or soil 2) were added into a series of 1000-mL flasks. Each received the amount of urea equivalent to 0.30 g N/kg soil, thoroughly mixed, and then moistened to 200 g water/kg soil, which represents the moisture levels under field conditions. Soils treated with urea were incubated at room temperature (25°C). At 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 14, 23, 33 and 48 days, respectively after urea application, three replicate soils were sampled for pH measurement and three other samples were extracted with 1 mol/L KCl solutions. The extracts were then filtered and analyzed for urea residues and exchangeable Cu and Zn.

The 100 g air-dried soil samples (soil 1 or soil 2), was placed in screw-top jars with volume of ca. 0.5 L (7-cm i.d., 12.5-cm long) and a soil depth of 2 cm. The soil was moistened with the addition of 20 g water/jar. The jars were designed to allow passage of air across the top of the soil sample and out of the jar. Each jar received a certain concentration of urea (equivalent to 80 mmol N/kg soil), and was incubated at room temperature. Following the application of fertilizers, jars were covered immediately and connected to an air flow. Incoming air passed through 2 L of 1 mol/L H₂SO₄ to remove ambient NH₃, then through 4 L of distilled water to humidify the air before entering the jar. Distilled water was added twice a week to replenish evaporated soil water. Air flow was maintained at 6 L/(min·jar) throughout the incubation period, corresponding to about 15 air volume exchanges per min. A flow meter was used to measure and adjust air flow through each jar. Air coming from sample jars passed into 100 mL of 0.32 mol/L H₃BO₃ solution contained in Erlenmeyer flasks for the absorption of NH₃. The collected NH₃ was titrated with 0.05 mol/L H₂SO₄ daily for two weeks.

1.3 Sampling analysis

Soil pH were measured with a glass probe at a soil: water ratio of 1:2 (*m/m*), the wet oxidation method of measuring organic carbon has been described by Carter (1993), and the cation exchangeable capacity (CEC) was determined using unbuffered 0.1 mol/L BaCl₂ (Hendershot and Duquette, 1986). The KCl-extractions were analyzed for urea residues (Mulvaney and Bremner, 1979). Measurements of Cu and Zn contents in various soil extractions were performed using an Atomic Adsorption Spectrophotometer with flame atomization (AA-240FS, Varian, USA). Ammonia volatilization was measured in a forced-draft system using covered jars swept with air (Al-Kanani et al., 1990). All reagents used were of analytical grade or better. Stock solutions of each metal for sample analysis were

Table 1 Basic physical and chemical properties of sample soils

Soil type	Site	pH	OM (g/kg)	CEC (cmol/kg)	Available nitrogen (mg/kg)	Urease activity (mg/(kg·hr))
Soil 1	Nongda	5.78	24.30	8.92	112	45.92
Soil 2	Donghu	5.50	18.69	11.03	91	30.72

OM: organic matter; CEC: cation exchangeable capacity.

obtained from the Research Center for Chinese Standard Materials. High purity water was prepared by double distillation of deionized water in a fused quartz still.

1.4 Statistical analysis

All experiments had three to five replicates. Means and standard errors were obtained for each set of measurements. Also, analyses of variance were performed on the data to compare the effect of the different treatments. The statistical package SAS (version 6.11, SAS Institute, Cary, NC) was used for the calculation of the SE and comparison of the means.

2 Results and discussion

2.1 Characterization of urea hydrolysis in soils

The common urea was quickly hydrolyzed both in the soil derived from river alluvial deposits in Dongting Lake Plain and red soil derived from quaternary red clay (Table 2), and was complete approximately 5 days after application. By comparison, the coated urea was hydrolyzed slowly, taking up to 14 days after application. It was shown that the coated material efficiently decreased the need for replenished water when the urea dissolved from the coated urea. Figure 1 shows that urea hydrolysis could cause high soil pH. For both soils, the pH peak occurred at day 5 after common urea application, which coincided with the urea hydrolysis; whereas the pH peak emerged at day 9 following coated urea use, which did not correspond to urea hydrolysis. This might indicate that nitrification started to occur in the coated urea treatments after 9 days, which counteracted the pH increase. Thus the pH peak was lower than that in the common urea treatment, and this process favored reduction of ammonia volatilization. The same phenomenon was also observed by Sun et al. (2004) in laboratory incubation experiments. The relationship between the accumulation of urea hydrolysis products and time could be well fitted by a logarithmic function (Table 3). This shows that the hydrolysis rate for the coated urea was lower than for the common urea, indicating that the coated urea can increase urea efficacy.

Table 3 Relationship between accumulation of urea hydrolysis content (%), Y and incubated days (t) after fertilizing with urea

Soil type	Fertilizer type	Formula	Correlation
Soil 1	Common urea	$Y = 30.089 + 37.093 \ln t$	0.969
	Coated urea	$Y = -5.127 + 33.286 \ln t$	0.901
Soil 2	Common urea	$Y = 41.562 + 33.637 \ln t$	0.970
	Coated urea	$Y = 5.307 + 34.865 \ln t$	0.990

Table 2 Urea residue in soils fertilized with urea (unit: mg/kg soil)

Soil type	Fertilizer type	Time after treatment						
		0	1 day	3 days	5 days	7 days	9 days	14 days
Soil 1	Common urea	642.82	408.89	236.00	42.22	BDL	BDL	BDL
	Coated urea	642.80	588.89	522.25	444.44	340.00	151.11	1.02
Soil 2	Common urea	642.81	351.11	176.04	3.33	BDL	BDL	BDL
	Coated urea	642.81	594.62	423.80	255.56	153.33	111.11	23.33

BDL: below the detection limit.

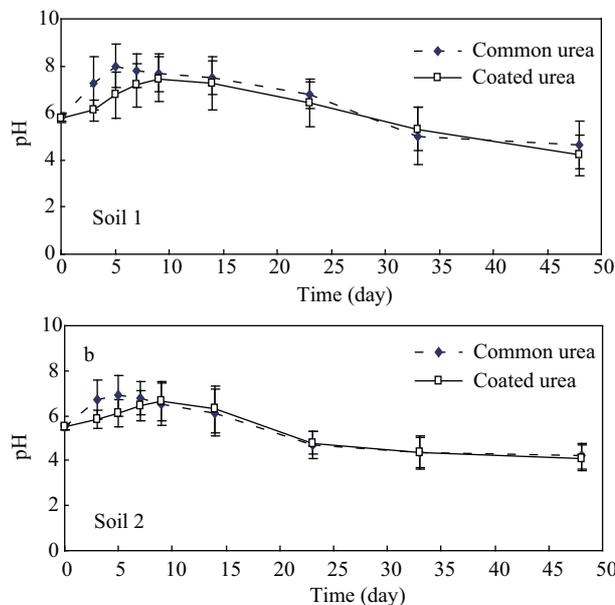


Fig. 1 Changes in soil pH after urea application to soils by adding 0.30 g N/kg soil. (a) changes in soil pH in soil 1 (the soil derived from river alluvial deposits in Dongting Lake Plain) by adding 0.30 g N/kg soil; (b) changes in soil pH in soil 2 (the red soil derived from quaternary red clay) by adding 0.30 g N/kg soil. The vertical bars represent the standard deviations ($n = 3$).

2.2 Characteristics of ammonia volatilization in soil after fertilizing with urea

Evidence of ammonia volatilization in the first day after fertilizing with common urea was observed in both soils, which became greater from day 5 to day 9, and then gradually reduced (Table 4). Compared with common urea application, the ammonia volatilization was smaller in both soils after fertilizing with coated urea. The rate of ammonia volatilization in two weeks after fertilizing with coated urea was 8% in soil 1 and 5.15% in soil 2, about half that observed after fertilizing with common urea. The time of the pH peak coincided with that of the ammonia volatilization peak for the common urea treatment, and the ammonia volatilization peak for fertilization with coated urea was lower than that with common urea in both soils. The time and size of the ammonia volatilization peak was different between soils fertilized with the same urea: the ammonia volatilization peak for soil derived from river alluvial deposits in Dongting Lake Plain was 43.59 mg/kg soil, higher than the 20.57 mg/kg soil observed for the red soil derived from quaternary red clay when both were fertilized with common urea. These differences were probably due to differing soil properties between the two types of soils.

Table 4 Daily volatilization of ammonia in soil after fertilizing with urea (unit: mg/kg soil)

Soil type	Fertilizer type	Time after treatment						Rate of ammonia volatilization (%)	
		1 day	3 days	5 days	7 days	9 days	11 days		14 days
Soil 1	Common urea	0.30 ± 0.11 a	5.06 ± 0.27 a	24.21 ± 4.26 a	43.59 ± 8.50 a	22.79 ± 2.96 a	12.44 ± 1.47 a	7.44 ± 1.70 a	16.20
	Coated urea	0.11 ± 0.04 a	0.71 ± 0.25 b	4.98 ± 1.13 b	10.46 ± 2.18 b	14.71 ± 1.98 a	11.08 ± 1.70 a	9.14 ± 1.73 a	8.00
Soil 2	Common urea	0.53 ± 0.17 a	10.12 ± 2.4 a	20.57 ± 3.54 a	16.04 ± 2.4 a	15.80 ± 1.77 a	6.61 ± 1.98 a	1.70 ± 0.57 a	10.93
	Coated urea	0.34 ± 0.06 a	0.83 ± 0.20 b	3.98 ± 0.99 a	8.37 ± 1.27 a	12.13 ± 2.69 a	6.61 ± 1.84 a	2.13 ± 0.85 a	5.15

Each value is the mean of three replicates ± SD. Value followed by the same letters are not significantly different among different treatment time at the 5% level by Duncan's multiple range test.

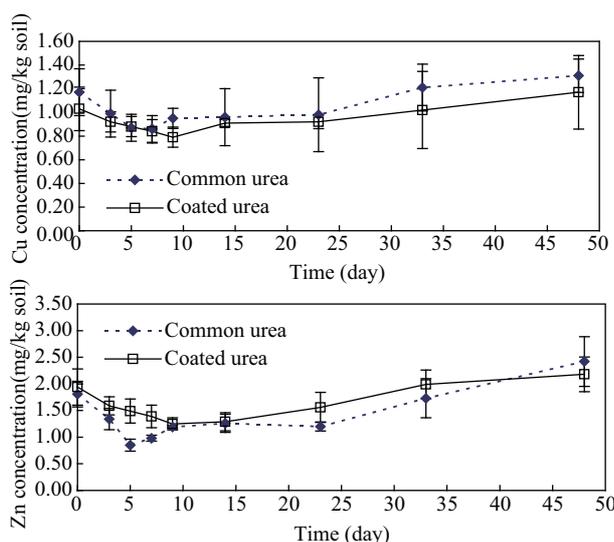


Fig. 2 Concentrations of extractable Cu and Zn in soil derived from river alluvial deposits in Dongting Lake Plain after two types of urea were applied at 0.30 g N/kg soil. (a) Concentrations of extractable Cu in soil derived from river alluvial deposits in Dongting Lake Plain after adding 0.30 g N/kg soil; (b) contents of extractable Zn in soil derived from river alluvial deposits in Dongting Lake Plain after adding 0.30 g N/kg soil.

2.3 Variation characteristics of exchangeable Cu and Zn in soil after fertilizing with urea

As shown in Fig. 2, the effects of urea application on exchangeable Cu and Zn followed the same trend. The exchangeable fraction of each element initially decreased as the pH value increased, and then increased with decreasing pH. The concentrations of exchangeable Cu and Zn correlated negatively with pH, and the result was consistent with that reported by Cakmak (2009). When the pH was 7.99, there was 0.79 mg/kg exchangeable Cu and 0.85 mg/kg exchangeable Zn in the soil derived from river alluvial deposits in Dongting Lake Plain. However, the concentrations of exchangeable Cu and Zn were generally lower for the common urea treatments than those with the coated urea because the peak pH of the common urea treatment was greater. The relationships between the concentrations of the two elements and the pH can be well fitted by a quadratic equation (Table 5).

The negative correlation between copper and pH is due to the fact that pH affects water-soluble copper, soil adsorption of copper and copper compounds' solubility. The data proves that in the range of pH 3.2–7.2, the water-soluble copper decreases gradually as the pH rises, but the soil adsorption and fixation of copper is stronger with rising pH. The relationship between pH and change of zinc in soil is relatively complicated. pH not only has a

Table 5 Relationship between concentrations of the two elements (Y) and pH (X) in the soil derived from river alluvial deposits in Dongting Lake Plain (Soil 1) after fertilizing with urea

Element	Fertilizer type	Formula	Correlation (n = 9)
Cu	Common urea	$Y = -0.0008X^2 - 0.075X + 1.4849$	-0.922**
	Coated urea	$Y = 0.0043X^2 - 0.0942X + 1.796$	-0.963**
Zn	Common urea	$Y = 0.054X^2 - 1.100X + 6.342$	-0.971**
	Coated urea	$Y = -0.027X^2 - 0.021X + 2.561$	-0.978**

direct impact on the solubility of various inorganic zinc compounds, but also affects the other properties of the soil, which influences the kinds of reaction mechanisms of zinc. The urea hydrolysis makes the pH value increase and when it rises to a certain value, the hydrolysis product HCO_3^- transforms into CO_3^{2-} , and CO_3^{2-} and Zn combine into zinc carbonate or $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$ which have low solubility. Chen et al. (2001) have demonstrated that it is favorable for zinc compounds to dissolve under weak acid conditions.

3 Conclusions

Based on these results, two conclusions can be derived. (1) ammonia volatilization was smaller for fertilization with coated urea in both soils, and the total volatilization of ammonia in two weeks after fertilizing with coated urea was about half that observed for common urea. It is evident that the coated urea efficacy was higher than that of common urea. (2) Soil pH increased after urea application, and the concentrations of exchangeable Cu and Zn were generally lower in the common urea treatments than in those with the coated urea because the peak pH of the common urea treatment was greater, therefore coated urea provided benefits for both plant production and human nutrition.

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