

Effect of Soil Water Contents on Urea Hydrolysis and Nitrification in a Newly Reclaimed Tidal Soils

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The effect of soil water content on the transformation potential of N compounds derived from hydrolysis of urea applied in a reclaimed tidal soils which was saline-sodic was observed to evaluate nitrification rates of urea. Soil samples were collected from Moonpo series at the newly reclaimed area in Saemanguem. For the transformation potential of N compounds from urea (46% N), newly reclaimed tidal soils (RS) were amended with urea at the rates of 0, 10, and 20 kg 10a⁻¹. With leachate obtained from the incubated RS in a leaching tube at 25°C, urea hydrolysis and nitrification were measured for a total of 30 days. The cumulative amounts of NO₃⁻-N in each of the four soils treated with urea was linear with time of incubation. Results showed that increase in pH occurred with increasing application rate of urea and volumetric water content due to hydrolysis of urea. The total N in the RS was decreased with incubation time, indicating that rates of urea hydrolysis was influenced by soil moisture conditions. Also, the cumulative amount of nitrate in RS gradually increased with increase in time of incubation.

Key words: Urea hydrolysis, Reclaimed Tidal Soils, Nitrification, Nitrate

Introduction

Surface applications of urea are most efficient when they are washed into the soil or applied to soils with low potential for volatilization. However, it is well known that leaching of fertilizer N is able to deprive the plant of much of its N supply before this can be fully utilized, especially on sandy soils.

Favorable economics of manufacturing, handling, storage, and transportation have made urea a very competitive source of fertilizer N. Urea, the principal form of dry fertilizer N as a convenient source and the highest nitrogen content of all solid nitrogenous fertilizers in common use, is solid, colourless, odorless, and non-toxic. The terms urea and carbamide are also used for a class of chemical compounds sharing the same functional group RR'N-CO-NRR', namely a carbonyl group attached to two organic amine residues. Example include carbamide peroxide, allantoin, and hydantoin. Urea is also used in many multi-component solid fertilizer formula-

tions. Urea, highly soluble in water, is therefore very suitable for use in fertilizer solutions, e.g., in 'foliar feed' fertilizers.

The transformation of urea generally occurs in two steps in soils: Urea is first converted to ammonium (NH₄⁺), and the NH₄⁺ is then converted to NO₃⁻. Both reactions are carried out by bacteria present in the soil. In most agricultural soils, ammonium (NH₄⁺) from fertilizer is quickly converted to nitrate (NO₃⁻) by the process of nitrification which is crucial to the efficiency of N fertilizers because the net effect is a conversion of fertilizer N from a form that is not normally subject to loss from soil (NH₄⁺) into a form that is readily lost by leaching or denitrification (NO₃⁻) (Rashidi and Al-Jabri, 1990).

Generally, high salt concentrations which attribute to substrate availability is one of the stress factors which influence soil microbial biomass (Sommers et al. 1978, Broadbent and Nakashima 1971). However, dissolution or hydrolysis of soil organic matter by high salt concentrations may offset some of the stresses placed on the microbial population from high salt concentrations in high saline or sodic soils (Vanessa et al., 2008; Pancholy and Rice, 1973). However, there are only a few species

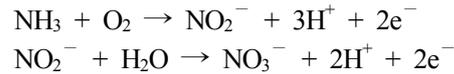
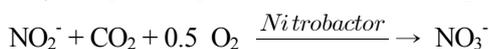
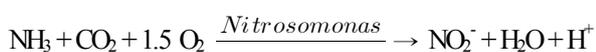
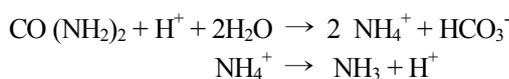
of nitrifying bacteria in high saline or sodic soils, resulting in that nitrification is much more sensitive to environmental conditions than are most other N transformations, which are carried out by a more diverse group of microorganisms.

Work by Eno and Blue (1957) showed that nitrification of NH_4^+ derived from urea in three sandy soils was much more rapid than nitrification of NH_4^+ from $(\text{NH}_4)_2\text{SO}_4$. Also the subsequent work by Martikainen (1985), de Boer et al. (1989), and McInnes and Fillery (1989) observed the rise in pH and a high concentration of ammonia (NH_3) that resulted from hydrolysis of urea by soil urease.

Understanding the fate of nitrogen species transformed from urea introduced into reclaimed tidal soil is important for nutrient management and environmental quality. However, there is little information available in literature on NO_3^- production by hydrolysis of urea amended in a reclaimed saline-sodic soil. Therefore, additional studies of N-fertilizer application are needed to make the most efficient use of urea in a reclaimed saline-sodic soils to supply food and energy. The present study was performed to evaluate nitrification rate of urea by hydrolysis of urea in a newly reclaimed saline-sodic soil under different soil water content.

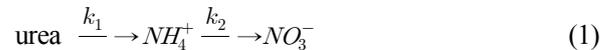
Theoretical

Urea applied in soil is generally hydrolyzed by the enzyme urease which is a naturally occurring enzyme that catalyzes the hydrolysis of urea to unstable carbamic acid. Rapid decomposition of carbamic acid occurs without enzyme catalysis to form ammonia and carbon dioxide (Tisdale et al., 1985; Benini et al., 1999). The ammonia will likely escape to the atmosphere unless it reacts with water to form ammonium (NH_4^+) according to the following reaction. Otherwise, the NH_4^+ , depending on soil pH, may form NH_3 , which can be volatilized at the soil surface, as represented in the following reactions:



Urease activity, greatest in the rhizosphere, varies depending on the plant species and the season of the year. In warm and moist soils, most of the urea rapidly transformed to NH_4^+ by hydrolysis of urea that is catalyzed by urease in several days. However, hydrolysis of urea can occur at temperatures down to 2°C and lower. This evidence of urease functioning at low temperatures suggests that a portion of fall or early winter-applied urea may be converted to NH_3 or NH_4^+ before the spring. High rates of urea fertilization in localized placement can create conditions restrictive to the action of urease. Significant concentrations of free NH_3 which can occur at pH values above 7 inhibit the enzymatic action of urease, because soil pH in the immediate vicinity of the urea source may reach values of up to 9.0.

Kumar and Wagenet (1984) reported that both urea hydrolysis and nitrification can be expressed with first-order reaction kinetics (Eq. [1]). A sequential reaction series can then be proposed in which



where k_1 and k_2 are the first-order rate constants (h^{-1}) describing enzymatic hydrolysis and nitrification, respectively.

Singh and Bajwa (1986) derived equation to describe the hydrolysis of applied urea in salt affected soils (Eq. [2]) with reaction coefficient (k) and $t_{1/2}$ for specific salt affected soils.

$$\ln(a-x) = \ln(a) - kt \quad (2)$$

where a = initial concentration of urea-N

x = time intervals in decrease of nitrogen concentration up to time t (days)

k = specific rate constant

Plotting the logarithms of the concentration of urea left unhydrolysed [$\log_{10}(a-x)$] against time 't', result shows linear relationships indicating that urea hydrolysis followed first order reaction kinetics for a given soil conditions.

Materials and Methods

The soils were collected from surface (0-30 cm) of the reclaimed soils (hereafter as RS) located at Saemangeum area in Kimgye Jeonbuk in Korea. The soils were air-dried and crushed to pass through a 2-mm screen. pH was determined with a glass electrode (soil : water ratio = 1 : 1); electrical conductivity (EC) using a saturated extract procedure described by Bower and Wilcox (1965); organic C by Walkley-black method (Jackson 1958); total N by Kjeldahl procedure described by Bremner (1965). Table 1 shows the physical and chemical properties of the soil samples used in this experiment.

For the incubation experiments to measure nitrification rate from urea, oven-dried reclaimed soil samples were thoroughly mixed with prilled urea at the rates of 0, 45, and 90 $\mu\text{g kg}^{-1}$ (quantity of urea was calculated to give equivalents of 0, 10, 20 kg N 10a^{-1}). 350 grams of RS-urea mixture was uniformly packed into 10 cm of an acryl tube (60 mm in diameter and 150 mm in length) while tapping the bottom of the column with a rubber mallet. Distilled water was then added to bring the three levels of volumetric soil moisture contents (0, 60, and 100% of the calculated porosity of RS).

The acryl tubes were placed in the incubation rack, and incubated at 25°C. After 1, 2, 3, 5, 7, 10, 15, 20, 25, and 30 days of incubation, the leachate to measure nitrate and total-N in RS were collected by placing the acryl tubes containing soil samples on a 250-mL suction flask while leaching with 100 mL of 0.01 M KCl in 4 to 5 increments. A suction was applied to give a vacuum of 6 kPa; The moisture contents of the columns during incubation at 25°C were adjusted by adding distilled water. Aliquots were taken for analysis of

NO_3^- -N and total-N (Bremner and Kenney 1966).

Results and Discussion

We observed changes in pH of the RS amended with and without urea under three volumetric water conditions for 0, 60, and 100% of porosity during 30 days of incubation. The results showed that changes in pH for the RS without urea amendment were very minimal compared to the changes in pH of the RS amended with urea while there was an initial increase in pH due to hydrolysis of urea (Fig. 1). The largest pH increase occurred with increasing application rate of urea and volumetric water content. The decline of the measured soil pH started rapidly after day 2 in the RS treated with 90 $\mu\text{g kg}^{-1}$ urea-N. However, the decline of the measured soil pH was slightly delayed with decreasing soil water content by day 4 for urea-N with 60% soil water content as shown in Fig. 1. On the other hand, pH measured on day 30 was increased with lower amount of urea-N as well as lower soil water content. The results indicated that increase and decrease of pH were closely related not only to the amount of urea amended in RS, but also to volumetric water content. With these changes of pH, we could assumed that the relative pH of RS with urea amendment was due to proton generation associated with nitrification as observed by Valdez et al., (2006). Magalhaes et al. (1987) also reported that hydrolysis of urea in soils strongly influence pH.

Figure. 2 shows the changes of total-N measured as remaining urea-N in the RS for three levels of soil moisture contents during 30 days of incubation. The total N including urea-N, NH_4^+ , and NO_3^- remained as

Table 1. Physical and chemical properties of reclaimed soil samples collected from Saemangeum area (Moonpo series).

Soil Series	pH	EC	TN	OM	Avail. P ₂ O ₅	Exchan-Cations				Soil particle distribution			
						K	Ca	Mg	Na	Sand	Silt	Clay	Texture
	(1:5)	(dS m ⁻¹)	----- mg kg ⁻¹	-----	-----	-----	cmol _c kg ⁻¹	-----	-----	-----	%	-----	-----
Moonpo	7.4	22.5	0.6	8.4	75	2.25	3.9	7.2	23.8	49.3	43.8	6.9	Loam

Table 2. Classification of treatment used in this experiment.

Category	Treatment								
	[†] RS0-0	RS45-0	RS100-0	RS0-60	RS45-60	RS100-60	RS0-100	RS45-100	RS100-100
Urea content ($\mu\text{g kg}^{-1}$ soil)	0	45	100	0	45	100	0	45	100
Water Content (θ_v , %)	0	0	0	60	60	60	100	100	100

[†]RS means a newly reclaimed tidal soil.

adsorbed and soluble in the RS was decreased with incubation time, indicating that rates of urea hydrolysis was influenced by soil moisture conditions.

The percentage of T-N remained in the RS increased as soil water content increased. For the treatment of 90 $\mu\text{g kg}^{-1}$ urea-N, T-N increased from 50.7 to 94.9% after 30 days of incubation (Table 2). Singh and Bajwa (1986) reported that the slow rate of urea hydrolysis in the salt-affected soils under investigation may be ascribed to the decrease in urease activity with increase

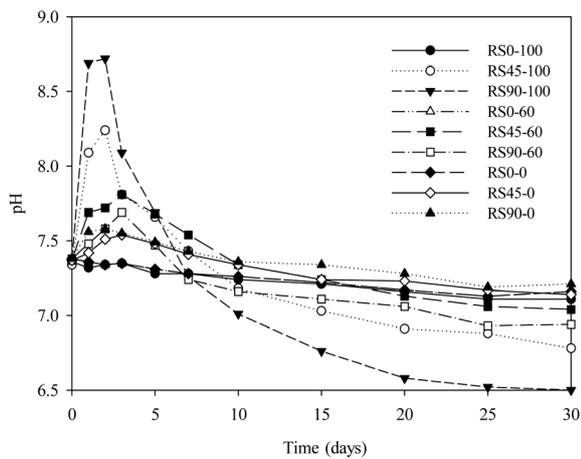


Fig. 1. Effect of the prilled urea concentrations on pH of RS during 30 days incubation at 25°C under three volumetric water contents.

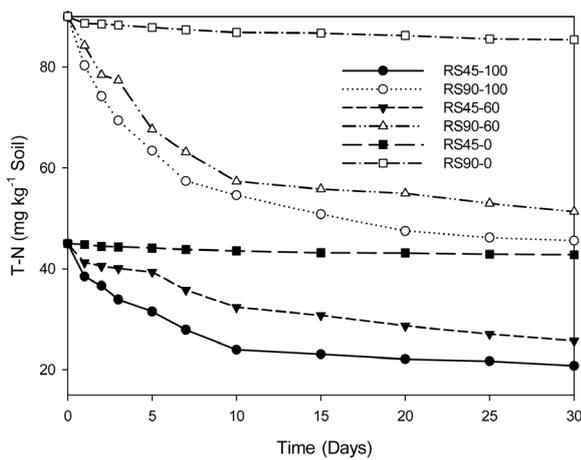


Fig. 2. Changes in T-N by hydrolysis of urea in recently reclaimed soils with amendment of the prilled urea at the rate of 0, 45, and 90 mg-N kg⁻¹ 25°C under three soil water condition for 30 incubation days.

in pH. Also they found that unhydrolysis in the unreclaimed sodic soils might be ascribed to the reduction of soil pH.

For cumulative concentrations of nitrate-N produced by hydrolysis of urea in recently reclaimed soils with amendment of the prilled urea, the cumulative amount of nitrate in RS gradually increased with increase in time of incubation (Fig. 3). The observed accumulation patterns of nitrate in RS were divided into two stages of I (relatively rapid) and II (slightly retarded) for a given soil moisture condition. The decrease in Total N and increase in cumulative amount of nitrate were greater with increasing soil water content while the time to reach the maximum amount of nitrate accumulated in RS took longer with increasing soil water content.

The differences in the accumulation of nitrate among different soil moisture contents represented that rates of urea hydrolysis was influenced by increasing volumetric water content due to increased diffusion of urea to the urease enzyme as investigated by Bouldin et al. (1991). Katyal and Carter (1988) also found that increased hydrolysis rates were closely related with increasing time of submergence. Especially in a newly reclaimed tidal soils containing high salt content, urea hydrolysis

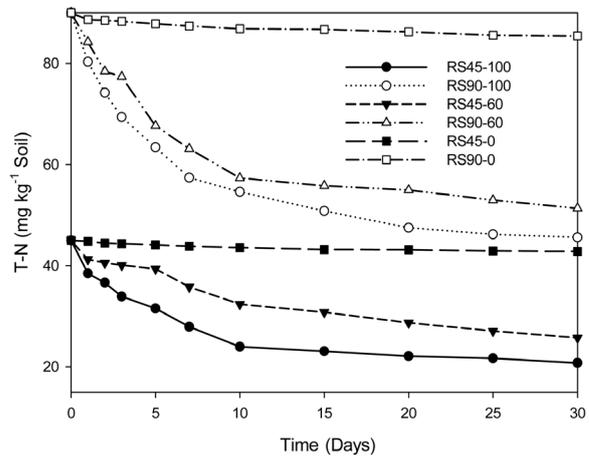


Fig. 3. Cumulative concentrations of nitrate-N in RS by hydrolysis of urea in recently reclaimed soils with amendment of the prilled urea at the rate of 0, 45, and 90 mg-N kg⁻¹ at room temperature under various water contents for 30 incubation days.

Table 3. Percentage of urea remained in RS after 30 days.

Incubation Period (day)	Urea remained in RS (%)					
	RS45-100	RS90-100	RS45-60	RS90-60	RS45-0	RS90-0
30	46.2	50.7	57.2	57.1	95.1	94.9

can be delayed by the salts due to reduction in urease activity (Frankenberger and Bingham, 1982; Galstyn, 1960).

However, there has been no systematic study of all of the factors involved in urea movement into and out of the soil, rates of urea hydrolysis, and movement of the ammoniacal N derived from urea hydrolysis into and out of the soil. Therefore, further work is needed for a satisfactory explanation.

Summary

Rashidi and Jabri (1990) reported that nitrification rate constants in calcareous saline soil were similar to the zero-order while the rate constants varied significantly among soils tested. They also found that the nitrification rate constants were smaller in high-salt-content soils and in soils with low N and clay contents compared with moderately saline, high-clay-content soils. Results obtained in this study (Fig. 2 and 3) showed that no significant differences and almost equal rates of nitrification were obtained from 45 and 90 $\mu\text{g kg}^{-1}$ soil. However, further work is needed for a satisfactory explanation because there has been few systematic study of all of the factors involved in urea hydrolysis in high saline-sodic soils of a newly reclaimed tidal soils.

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