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Urea Transformations in Flooded Soil.

Chawalit Hongprayoon
Louisiana State University and Agricultural & Mechanical College

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Urea transformations in flooded soil

Hongprayoon, Chawalit, Ph.D.

The Louisiana State University and Agricultural and Mechanical Col., 1992

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UREA TRANSFORMATIONS IN FLOODED SOIL

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Agronomy

by

Chawalit Hongprayoon
B.S., Kasetsart University, 1974
M.S., Kasetsart University, 1980
December, 1992

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ABSTRACT

Laboratory incubation studies were conducted to measure adsorption, movement, and transformations of urea and hydrolyzed ammoniacal N in flooded soil columns. Urea was added to the floodwater (750 mg N L^{-1} , equivalent to 150 kg N ha^{-1}) of Crowley silt loam soil columns and urea diffusion and urea hydrolysis were measured. Subsequent $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ distribution after urea application and hydrolysis were measured over a 30 d period under aerobic and anaerobic conditions. Effects of percolation rates (0, 1, and 2 cm d^{-1}), and the use of urease inhibitor, N-(n-butyl) thiophosphoric triamide (NBPT), on movement and transformations of urea in flooded soil columns were also investigated over a period of 0.5, 1, and 2 d.

Urea adsorption by the soil increased with increasing concentration of added urea-N and adsorption coefficients ranged from 0.037 to 0.064 but modeling found adsorption to be too small to be an important factor in urea movement and hydrolysis. Urea hydrolysis rates in the flooded soil columns increased with time and followed first-order reaction kinetics. Rate constants measured in the soil varied from 0.036 to 0.288 h^{-1} . The diffusion coefficient for both N forms (urea and NH_4^+) was estimated to be $3.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ in the flooded soil columns. The distribution of $\text{NH}_4^+\text{-N}$ in soil columns under aerobic and anaerobic conditions did not show distinct or different patterns. Percolation rates affected the movement of urea into deeper soil layers and had little effect on the movement of $\text{NH}_4^+\text{-N}$ (hydrolyzed from urea) in the soil except

at the highest rate of percolation 2 d after urea application. Addition of NBPT with urea in the floodwater drastically retarded urea hydrolysis and enhanced the effect of percolation on the transportation of urea into soil layers. The average percentage inhibition of NBPT on urea hydrolysis was 81.5 and 56.7% at 1 d and 2 d after urea application, respectively.

INTRODUCTION

Importance of urea

The continuous increase in human population stresses the need for increasing world food production. Rice is one of the main food crops which has high potential for increasing production, especially in Asia where 90-95% of the world's rice is produced (Pathak and Gomez, 1991). Nitrogen is the most limiting nutrient for rice growth and yield throughout the rice growing regions of the world. Application of N fertilizer is normally required to maximize rice yield. It also appears that the utilization of N by rice in flooded soils is even lower than that measured for arable crops, because of additional N loss pathways present under flooded soil conditions (Wells and Turner, 1984). Research to improve the uptake efficiency of fertilizer N has moved toward an understanding of the loss pathways and of manipulating N fertilizers to maximize plant uptake and minimize loss. However, suitable and effective use of N is concerned not only with maximizing yield but also the world environment since unused fertilizer N may contribute to environmental pollution (Craswell and Vlek, 1979; Pratt, 1984).

Urea is the dominant N fertilizer used for rice culture in flooded soil. Use of urea in rice agriculture has increased dramatically during the past 20 years (Stangel, 1984; Voss, 1984). The advantages of urea include high N content, low cost of manufacture, transportation, storage and distribution; high solubility in water, and ease of handling (Mulvaney and Bremner, 1981). Using urea in flooded rice agriculture, however, has problems associated with high losses of N through its transformation

processes. Ammonia volatilization and denitrification are considered to be the two major possible losses of N from rice soils. Leaching under flooded systems may also cause high loss of N of applied urea in some areas. Sherma et al.(1989) reported that water percolation rates of 10 mm d⁻¹ leached as much as 79 kg N through the soil profile during the 11 week experiment. Information on transformations and distribution of urea under varying percolation rates are still insufficient.

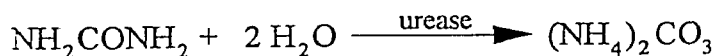
Flooded environment

Submergence of soil creates unique chemical and biological conditions, which markedly influence N transformations. The major effect of the floodwater is that it restricts O₂ diffusion creating an aerobic-anaerobic system where nitrification-denitrification processes can occur. Restriction of O₂ diffusion into the soil, inhibits aerobic N transformation, primarily nitrification, but enhances anaerobic N transformation, primarily denitrification (Patrick and Reddy, 1976). Nevertheless, aerobic N transformations are not completely inhibited. Oxygen diffuses from the atmosphere to the soil surface or moves through the plant to the rhizosphere. Algal photosynthesis in the floodwater can also cause some oxygenation of the floodwater and soil surface. The degree of oxygenation and thickness of the oxidized layer at the soil surface depends on the oxygen concentration of the floodwater and the soil's O₂ consumption rate. The oxygenated layer usually ranges from 0 -3 cm. The oxidized and reduced soil layers, in contact with each other, provide an ideal environment for simultaneous nitrification and denitrification, resulting in substantial loss of N through

the denitrification process (Patrick and Reddy, 1976). The presence of floodwater also drastically alters soil conditions affecting other N transformations and loss mechanisms such as urea hydrolysis, diffusion, leaching, and surface water run-off. The transformations of applied urea in waterlogged soil vary widely depending on cultural practices, environmental conditions, and soil properties (Wells and Turner, 1984).

Transformations of urea

When applied to moist soil, urea can be hydrolysed rapidly to CO_2 and NH_3 by the activity of the urease enzyme:



Soil urease may be derived from plants or soil microorganisms and is readily found in most soils (Bremner and Mulvaney, 1976; Hoult and McGarity, 1986; Voss, 1984). Pettit et al.(1976) reported that native urease in soil is remarkably stable under conditions which rapidly inactivate jack bean urease. Stability of urease may due to the adsorption of the enzyme onto organic-clay complexes (Boyd and Mortland, 1985; Pettit et al.,1976). Activity of this enzyme is affected by many soil parameters. Several investigations reported that urease activity in soil increases as soil organic carbon, cation exchange capacity, or clay content increases (Mulvaney and Bremner,1981;

Lloyd and Sheaffe, 1973; Vlek and Carter, 1983). Hydrolysis of urea resulting in accumulation of NH_4^+ and an increase in pH can lead to loss of NH_3 and/or increase in soil NO_2^- concentrations (Craswell and Vlek, 1979; Kissel et al., 1988). Estimates of NH_3 -N loss from flooded rice soils range from <1 to >50% of applied urea-N (De Datta et al. 1991; Voss, 1984). Cultural practices, soil and environmental conditions affect the amount of loss of volatilized NH_3 . Concern that high loss of N occurs during urea hydrolysis from urea hydrolysis had led researchers to attempt to reduce loss by using urease inhibitors. Several compounds found to have an inhibiting capacity on soil urease includes inorganic salts of Ag, Hg, and Cu; dihydric phenols; and quinones such as hydroquinone and *p*-benzoquinone. Recently, phenylphosphorodiamide (PPD) and *N*-(*n*-butyl)thiophosphoric triamide (NBPT) have been found to be effective inhibitors of urease activity (Beyrouthy et al., 1988; Bremner et al., 1991; Lu et al., 1989; Voss, 1984). Lindau et al. (1989) showed that PPD was more effective under reducing conditions and NBPT was more effective in inhibiting urea hydrolysis under oxidizing conditions. Creason et al. (1990) found that the inhibitory activity of NBPT was due to formation of its oxon analog. The value of urea inhibitors lies in their ability to slow urea hydrolysis and reduce NH_3 loss. In using these inhibitors, however, additional research has to be done to develop management practices to reduce N loss from the soil system (Craswell and Vlek, 1979; Voss, 1984).

Delaune and Patrick (1970) have shown that the urea hydrolysis rate in flooded soils is about the same as in aerobic soils. They also found the soil, rather than the floodwater, is the main site of hydrolysis. The rate of urea hydrolysis is likely to have

a major influence on other N transformation processes (Craswell and Vlek, 1979). The lower rate of hydrolysis in floodwater may allow more urea to diffuse into the soil. Since urea is only weakly adsorbed to soil colloids it can move more readily than NH_4^+ into lower soil layers by diffusion and/or percolation. Translocation of urea into reduced soil is considered to be beneficial because NH_4^+ from urea hydrolysis has less chance to be oxidized to NO_3^- and denitrified (Reddy and Patrick, 1984). The movement of urea into the soil has another advantage: it reduces the loss of urea by surface water run-off. The distance that urea can move into the soil depends upon the rate of urea hydrolysis and soil properties which affect percolation and urea adsorption rates (Rao and Ahmad, 1983; Rachhpal-Singh and Nye, 1984). Nevertheless, the high translocation rate of urea-N into coarse textured soils may cause leaching from the rhizosphere system and pollute the underlying groundwater environment.

The urgency and importance of the N inefficiency problem has stimulated a great deal of research to develop more efficient fertilizer management practices. Progress has been limited by the lack of complete knowledge of the fate of applied N not utilized by the crop. The understanding of translocation and transformations of N from applied urea is essential to develop practical agricultural techniques to prevent losses and increase fertilizer efficiency in lowland rice culture.

Research objectives

The principle objectives of the research were to:

- 1) investigate the rate of urea diffusion and urea hydrolysis in flooded soil columns.

- 2) determine the distribution of NH_4^+ and NO_3^- in flooded soil columns under aerobic and anaerobic conditions after urea application.
- 3) study the effects of percolation rates and the use of a urease inhibitor on movement and transformations of urea in flooded soil columns.

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CHAPTER I

UREA TRANSFORMATIONS IN FLOODED SOIL COLUMNS

Introduction

Rice is the staple food of ≈ 40 to 50% of the world's people. World rice acreage has increased at an annual rate of about 1% during the past 50 yr (1935-1985) and the total harvested area is estimated at 146 million ha (De Datta, 1988). Approximately 90% of the world's cultivated rice area is in Asia, of which 53% is irrigated, producing $> 70\%$ of the world's rice crop. Asian population growth demands the rice production must increase about 3% annually through crop intensification, improvement in rice varieties, increased fertilizer usage, and increased fertilizer-use efficiency (De Datta, 1988).

Nitrogen accounts for $\approx 67\%$ of the fertilizer (N + P + K) applied to rice crops and $> 90\%$ of the total fertilizer-N consumption by rice is in the urea form (Vlek and Byrnes, 1986). Flooded rice uses applied N inefficiently and recovery by the crop can be as low as 20 to 40% because of poor management practices, leading to extensive N losses (De Datta, 1988). In addition, N is difficult to manage in flooded soil systems due to the complicated transformations it undergoes. Submergence of rice soils results in the formation of a thin, oxidized, soil surface layer in contact with an underlying reduced zone. The chemical, biological, and physical properties of the two distinct soil

layers strongly influence urea transformations and N losses from flooded rice soils (Reddy and Patrick, 1984). Knowledge of the basic urea-N pathways and transformations is needed to improve fertilizer-use efficiency in lowland rice.

Urea movement and behavior has been researched extensively under upland soil conditions but reported effects of soil submergence are scarce, varied, and poorly understood (Bremner and Mulvaney, 1978; Keeney and Sahrawat, 1986). Rao and Ahmad (1983) studied urea adsorption in 19 Trinidad soils and concluded that soil organic C, clay content, and CEC significantly affected urea adsorption. Soils grouped in the high-urea-adsorption class were high in organic C and 2:1 clay minerals. Sadeghi et al. (1989) measured the diffusion coefficient of urea in seven upland soils and noted that reduction of soil water content (24-34%) caused urea diffusion coefficients to be approximately two times lower. Rachhpal-Singh and Nye (1984, 1986) investigated urea and ammoniacal-N diffusion in unsaturated soil diffusion cells and developed predictive mathematical models to describe solute movement and loss from the soil. Good agreement was found between experimental and predicted values of NH_3 volatilization, urea diffusion, and $\text{NH}_4\text{-N}$ diffusion.

A laboratory study by DeLaune and Patrick (1970) demonstrated that the main site of urea hydrolysis was in the soil and not the floodwater. After 30 hours of incubation, 3 and 64% of the added urea was hydrolyzed in the floodwater and soil, respectively. Additional studies by Gould et al. (1973) also showed that soil water content had little effect on urease activity, but other researchers have found hydrolysis rates to increase with increasing soil water up to field capacity (Vlek and Carter, 1983).

Savant et al. (1985) observed that depletion of O_2 in submerged soils retarded urea hydrolysis and the order of hydrolysis rate was : oxidized soil > reduced soil > floodwater. Lindau et al. (1989) conducted laboratory experiments and measured urea hydrolysis rates in four rice soil suspensions. Hydrolysis rates followed first-order kinetics and rate constants in the calcareous soil were much higher than in the acid soils.

The objectives of this laboratory study were to measure adsorption, diffusion, and hydrolysis of applied urea, and its distribution in flooded soil columns.

Materials and Methods

The soil used in the incubation studies was a Crowley silt loam collected from the Rice Research Station, Crowley, LA. Soil properties included : pH of 5.8 (1:1, soil/water ratio), CEC of 9.4 cmol kg⁻¹ of soil, 7.0 g total C kg⁻¹, 0.8 g total N kg⁻¹, 11 % clay, and 71 % silt. Approximately 80 kg of soil was dried, ground, and sieved through a 2-mm mesh screen and then thoroughly mixed.

Urease Inhibition

To prevent the hydrolysis of urea in flooded soil columns in the study of urea diffusion columns, the efficiency of the urease inhibitor was tested using autoclaved and nonsterilized soil. Three replications of 20 g of autoclaved soil (autoclaved at 121 °C, 15 psi for 2 h) or nonsterilized soil were equilibrated in 250 ml Nalgene bottles with 20 ml of 260 mg N L⁻¹ sterilized urea solution. Filter sterilized urease inhibitor, N-(n-butyl) thiophosphoric triamide (NBPT), was thoroughly mixed into the soil to the concentrations of 0, 1, 2, 5, and 10% (w/w) of urea added. The mixtures were incubated at 30 °C for 0.5, 1, 2, 4, 6, and 8 d. At the end of each incubation period, each treatment was extracted with 2M KCl and urea concentration was determined by the diacetyl monoxime method (Bremner, 1982).

Urea Adsorption

To measure urea adsorption, 40 g of autoclaved soil (autoclaved at 120°C, 15 psi for 2 h) was equilibrated with 20 mL of sterilized deionized water containing the urease inhibitor NBPT (214 mg L⁻¹) and increasing concentrations of standardized urea-N solutions (50, 86, 254, 512, 750, and 1000 mg N L⁻¹). Each urea-N treatment was replicated three times. From a previous experiment, NBPT at a concentration of 10% of urea (w/w) was known to effectively stop all urea hydrolysis in autoclaved soil for 6 d. The urea plus NBPT plus soil solutions were thoroughly mixed and incubated at 30°C for 48 h. Soil suspensions were then vacuum filtered (Whatman no. 42) and urea concentrations determined on a suitable aliquot of solution extract. Urea concentrations were determined by the colorimetric method (Bremner, 1982).

Urea Diffusion and Hydrolysis

Thirty-six Plexiglas columns (30-cm length by 7.5-cm i.d.) with a 2-cm-thick paraffin-petroleum jelly base (4:1 ratio) were constructed and 1 kg of soil uniformly packed into each column (bulk density = 1.3 g cm⁻³). To measure urea diffusion, autoclaved soil, sterilized water, and NBPT (161 mg L⁻¹) were added to 12 columns. An additional 12 columns packed with nonsterilized soil were used to investigate urea diffusion plus hydrolysis, and the remaining cores were controls (no urea added). Soil columns were slowly filled from the base until the columns were saturated and a 2-cm floodwater depth established. Columns were incubated for 3 d at 30°C before urea-N was added. After incubation, the floodwater was removed and replaced by a urea

solution (750 mg N L^{-1}) to a depth of 2 cm. The urea-N solution concentration corresponds to a urea soil application rate of 150 kg N ha^{-1} , which is commonly added to Crowley silt loam soil under flooded rice production. The soil columns were again incubated in the dark at 30°C for 0, 0.5, 1, 2, 4, and 6 d. At the end of each incubation period, duplicate columns for each treatment were sampled. Floodwater was removed and each column was sectioned into seven soil layers at depth of 0.5, 1.0, 2.0, 3.0, 5.0, 7.5, and 10 cm from the surface. Weight of floodwater and each soil section were recorded and the soil water content determined (105°C). Urea was extracted from the soil sections by shaking for 1 h with 2M KCl (1:10 soil/KCl ratio) containing $5 \mu\text{g mL}^{-1}$ of phenylmercuric acetate (PMA). Soil solutions were filtered and the solution extracted was analyzed for urea-N content. Urea in the floodwater and soil-section extracts was determined colorimetrically (Bremner, 1982).

Results and Discussion

Urea Hydrolysis Inhibition

In a preliminary test on urea hydrolysis inhibition, it was found that addition of NBPT at the concentration of 5 to 10% of added urea (w/w) together with autoclaved soil completely inhibited urea hydrolysis up to 6 days of incubation (Figure 1). Neither NBPT nor autoclaved soil alone completely inhibit urease activity. Autoclaved soil showed a better inhibiting effect than NBPT, however, after 4 d of incubation, only 5.5% of the added urea remained in the system (data not shown).

Urea Adsorption

To mathematically describe the relationship between urea adsorption by the soil and the solution urea equilibrium concentration, the empirical Freundlich and Langmuir equations are often used. Both equations can be simplified for specific conditions and an adsorption equation based on a simple proportionality can be derived (de Hann and Zwerman, 1976). This simplified equation was applied to the urea adsorption data obtained in this study.

$$x/m = K_{us} C_o$$

or

$$K_{us} = (x/m)/C_o$$

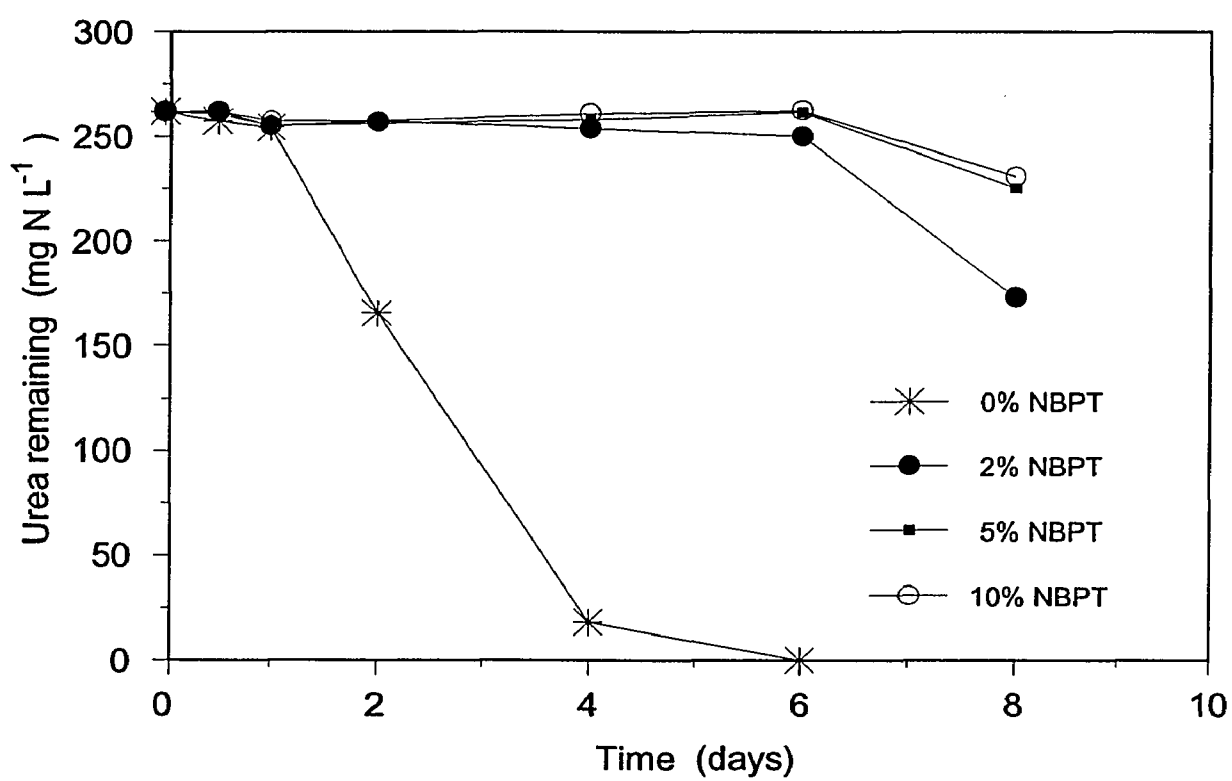


Fig. 1. Effect of NBPT concentrations on inhibition of urea hydrolysis in autoclaved flooded Crowley silt loam soil.

Where $x/m = \mu\text{g urea-N adsorbed g}^{-1} \text{ soil}$, $C_o = \text{equilibrium concentration of urea in solution } (\mu\text{g urea-N mL}^{-1})$, and $K_{us} = \text{distribution coefficient}$. The logarithmic plot of x/m against $\log C$ is shown in Figure 2 with a high concentration between both parameters and R^2 was 0.99.

The results of urea adsorption study are shown in Table 1. Values of K_{us} ($\times 100$) increased with increasing concentration of added urea-N solution, with an average value of about 5.1. In a soil column with a volumetric water content of 0.5 and a bulk density of 1, the ratio of urea in solution to that sorbed on the soil would be 10. These data indicated that urea adsorption by the Crowley silt loam was low and of minor significance. The urea-adsorption values determined in this study were low compared to those reported by Rao and Ahmad (1983). Urea adsorption was measured in Trinidad soils and reported K_{us} ($\times 100$) values ranged from 12 to 93, depending on soil type. In the Trinidad soils, urea adsorption increased with increasing soil CEC, organic C, and clay content. Urea adsorption may play a more significant role in urea movement in rice soils other than Crowley silt loam, and should be measured when urea transformations are investigated.

Urea Diffusion and Hydrolysis

Urea diffusion in flooded soil columns is shown in Figure 3 and Table 3 and 4, where urea concentrations are expressed on a soil-water basis. At the 0.5-d sampling, the urea front had diffused down to the 1-to 2-cm soil layer, which contained an average urea-N concentration of 23.9 mg L^{-1} soil water. At 1 d, the front had moved

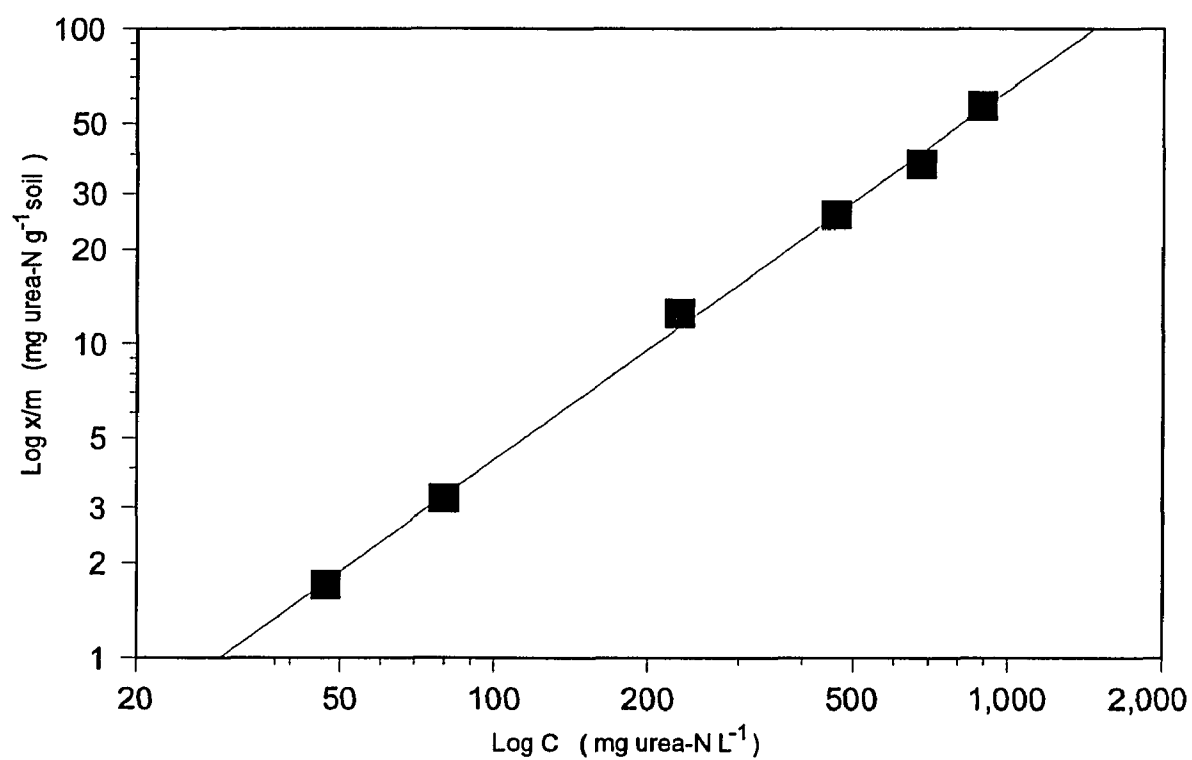


Fig. 2. Isothermal equilibrium adsorption of urea-N by Crowley silt loam soil.

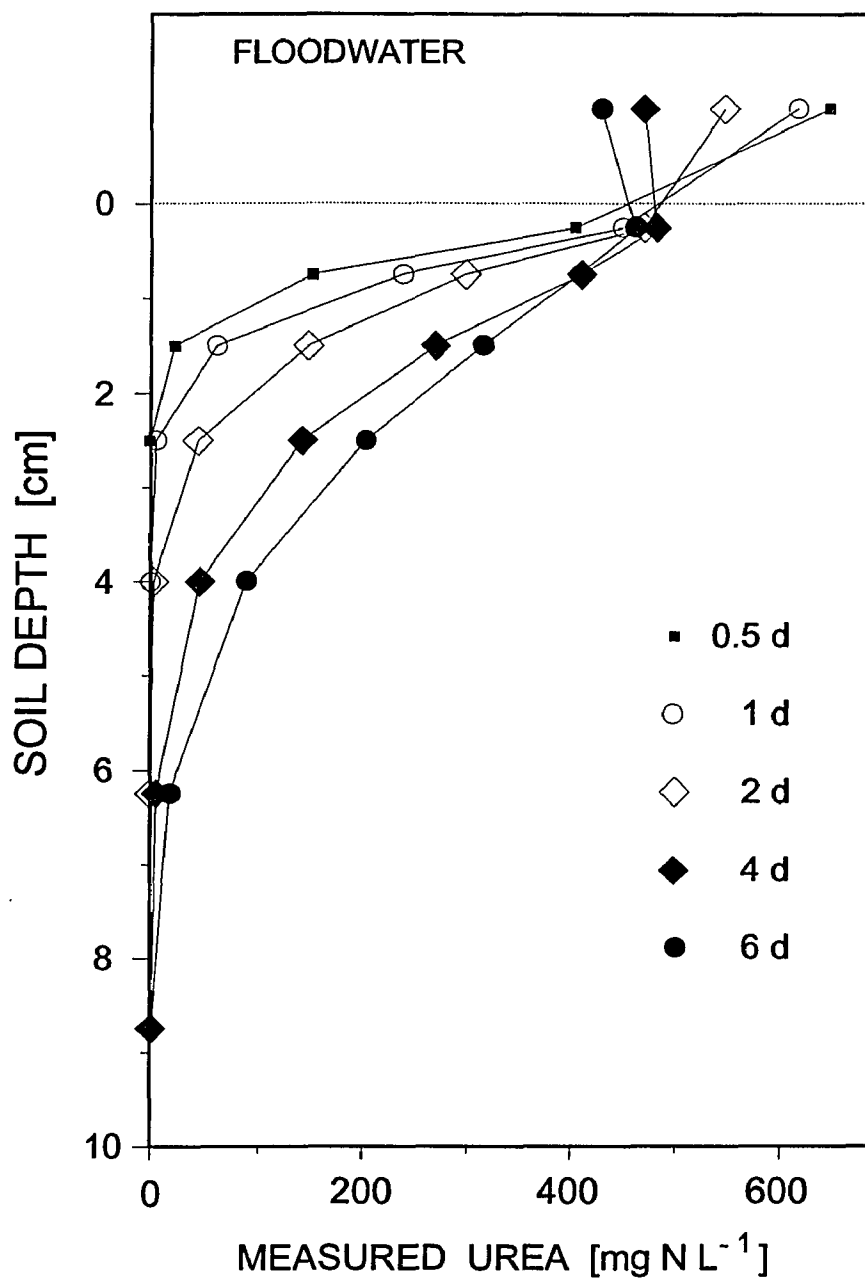


Fig. 3. Distribution of urea due to diffusion in flooded Crowley silt loam columns over a 6 d period.

Table 1. Effect of urea-N solution concentration on the urea adsorption coefficient.

Concentration of added urea	Urea adsorption coefficient *
mg N L ⁻¹	(× 100)
50	3.7 ± 2.1
86	4.0 ± 3.0
254	5.4 ± 0.3
512	5.5 ± 0.1
750	5.5 ± 0.6
1000	6.4 ± 0.9

* Each value represents the average and standard deviation of three observations.

Table 2. Estimated rates of urea hydrolysis in soil and overlying water.

Time interval	Rate of hydrolysis	
	soil	water
h	mol s ⁻¹	
0 - 12	1 × 10 ⁻⁵	2 × 10 ⁻⁷
12 - 24	6 × 10 ⁻⁵	2 × 10 ⁻⁶
24 - 28	8 × 10 ⁻⁵	4 × 10 ⁻⁶

Table 3. Concentration of urea-N in autoclaved flooded Crowley silt loam soil columns containing NBPT during 6 d after urea addition.

layer (cm)	urea concentration (mg N L ⁻¹)					
	0 d	0.5 d	1 d	2 d	4 d	6 d
floodwater	750.0	659.5	628.8	558.1	480.1	437.5
0 - 0.5	0.0	413.4	458.7	479.4	491.9	470.9
0.5 - 1	0.0	157.2	244.4	306.0	419.1	417.0
1 - 2	0.0	23.9	64.8	153.5	277.0	322.7
2 - 3	0.0	0.0	6.0	46.9	147.9	209.5
3 - 5	0.0	0.0	0.0	3.4	48.6	93.2
5 - 7.5	0.0	0.0	0.0	0.0	5.9	19.0
7.5 - 10	0.0	0.0	0.0	0.0	1.4	1.6

Table 4. Total content of urea-N in autoclaved flooded Crowley silt loam soil columns containing NBPT during 6 d after urea addition.

layer (cm)	urea content (mg N)					
	0 d	0.5 d	1 d	2 d	4 d	6 d
floodwater	67.7	59.0	58.2	53.5	43.7	41.2
0 - 0.5	0.0	5.5	5.0	5.7	6.3	5.4
0.5 - 1	0.0	1.6	3.4	3.5	5.3	4.6
1 - 2	0.0	0.5	1.6	3.6	6.3	6.8
2 - 3	0.0	0.0	0.1	1.1	3.4	4.5
3 - 5	0.0	0.0	0.0	0.1	2.1	3.9
5 - 7.5	0.0	0.0	0.0	0.0	0.3	1.0
7.5 - 10	0.0	0.0	0.0	0.0	0.1	0.1

to the 2-to 3-cm layer ($6.0 \text{ mg urea-N L}^{-1}$) and, at 2 d, urea had diffused into the 3- to 5-cm saturated soil layer (3.4 mg N L^{-1}). Urea continued to move down the soil column and, at 4 and 6 d after urea addition to the floodwater, urea was detected in the 7.5- to 10-cm section with an average solution concentration of 1.4 and 1.6 mg urea-N L^{-1} , respectively. At the 0-, 0.5-, 1-, and 2-d samplings, urea-N concentration decreased from the floodwater layer through the soil profile but this was not the case at 4 and 6 d. On these two sampling dates, the 0- to 0.5-cm section had higher urea-N concentration compared with the overlying floodwater (Fig. 3). This was probably due to soil adsorption of urea-N, which is supported by the initial adsorption experiment (Table 1). To verify that hydrolysis was not occurring during the urea-diffusion experiment, a mass balance for urea-N was calculated at the end of each sampling date based on urea-N content of the floodwater and soil sections. At time zero, 67.7 mg urea-N was added to the floodwater layer and total urea-N content was found to be constant up to 6 d. At 6-d sampling, the average urea-N content of the three treatment cores was 67.5. The mean and standard deviation of the urea-N content of the soil cores during the 6 d was 67.5 ± 0.5 demonstrating that urea was conserved during this sampling period.

The results of the urea diffusion plus hydrolysis experiment in nonsterile soil columns is displayed in Figure 4 and Table 5 and 6. Urea-N was not detected in any soil sections or floodwater at 4 d. At the end of day 1, 61.9% of the added urea-N remained unhydrolyzed, compared with only 21.4% on day 2 which was found only in the floodwater. During the 6-d experiment, urea was never detected in the layer deeper

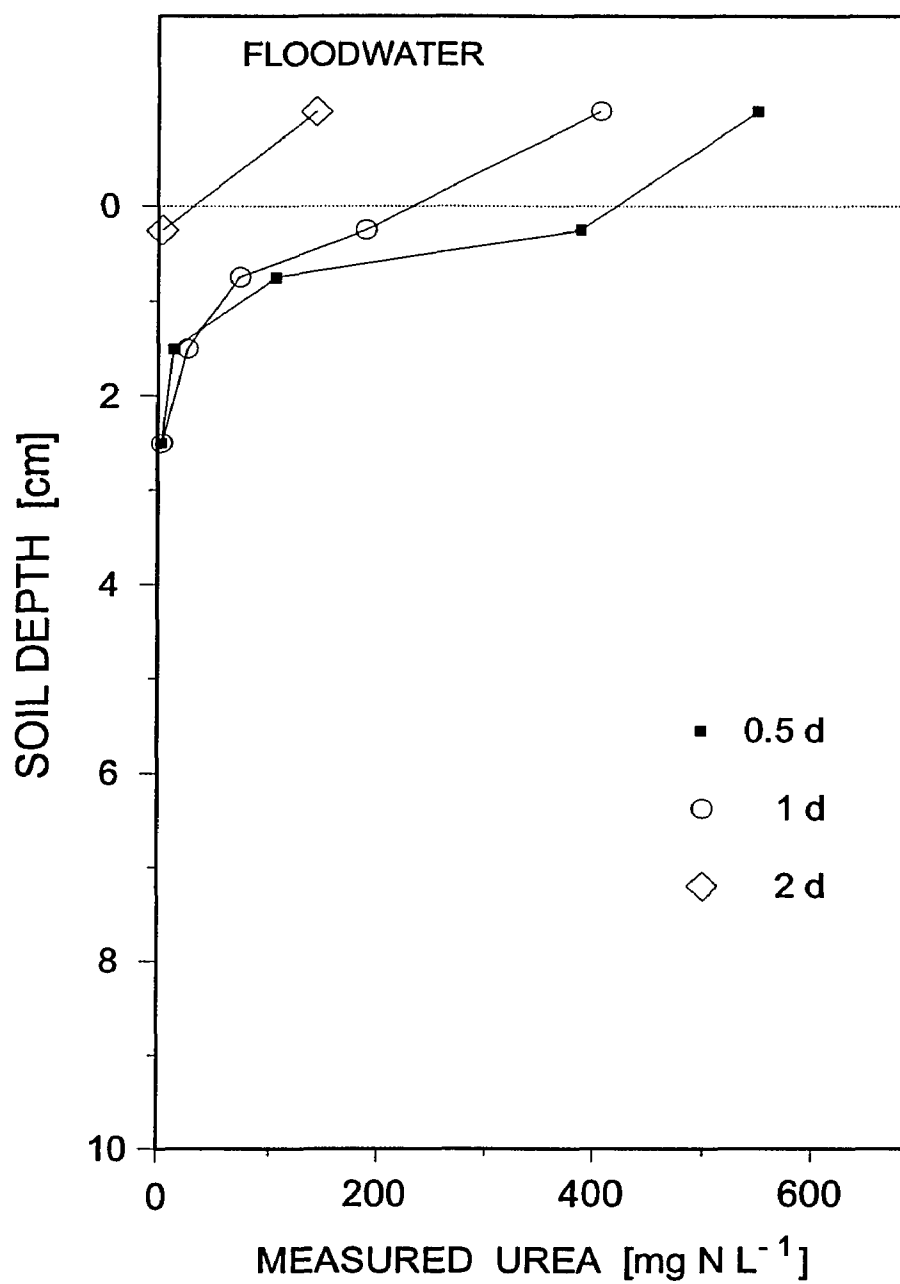


Fig. 4. Distribution of urea due to hydrolysis and diffusion in flooded Crowley silt loam columns over a 2 d period.

Table 5. Concentration of urea-N in nonsterilized flooded Crowley silt loam soil columns incubated without NBPT during 2 d after urea addition.

layer (cm)	urea concentration (mg N L ⁻¹)			
	0 d	0.5 d	1 d	2 d
floodwater	750.0	558.5	411.6	144.3
0 - 0.5	0.0	393.0	190.7	0.2
0.5 - 1	0.0	107.0	73.0	0.0
1 - 2	0.0	10.8	23.8	0.0
2 - 3	0.0	0.0	0.0	0.0
3 - 5	0.0	0.0	0.0	0.0
5 - 7.5	0.0	0.0	0.0	0.0
7.5 - 10	0.0	0.0	0.0	0.0

Table 6. Total content of urea-N in nonsterilized flooded Crowley silt loam soil columns incubated without NBPT during 2 d after urea addition.

layer (cm)	urea content (mg N)			
	0 d	0.5 d	1 d	2 d
floodwater	67.7	51.1	38.3	14.5
0 - 0.5	0.0	5.4	2.1	0.0
0.5 - 1	0.0	1.3	0.9	0.0
1 - 2	0.0	0.2	0.6	0.0
2 - 3	0.0	0.0	0.0	0.0
3 - 5	0.0	0.0	0.0	0.0
5 - 7.5	0.0	0.0	0.0	0.0
7.5 - 10	0.0	0.0	0.0	0.0

than the 1-to 2-cm soil section. At 0.5 and 1 d after urea addition, the average urea-N soil solution concentration in 1- to 2-cm section was 10.8 and 23.8 mg urea-N L⁻¹, respectively. The results demonstrate that urea applied to the floodwater rapidly diffuses into the soil profile and is hydrolyzed. Here we are assuming the soil is the main site of urea hydrolysis which is supported by the work of DeLaune and Patrick (1970). In addition, Lindau (1986, unpublished data) also showed similar results. In that study, floodwater was removed from a rice field (Crowley silt loam) 2 weeks after permanent flood and urea-N added to assess urease activity. Air was continually bubbled through the stirred floodwater containing 100 mg urea-N L⁻¹. Two days after N addition $\approx 50 \text{ g kg}^{-1}$ of the urea had been hydrolyzed, which agrees with 30 g kg^{-1} in the DeLaune and Patrick (1970) studied.

The data collected from the autoclaved soil columns were used to estimate the urea diffusion coefficient after urea addition to the floodwater. Bouldin et al. (1991) used finite-difference equations to describe the urea movement and transformations. Measured values of urea concentration in the sectioned soil layers were regressed and compared with the values calculated with the model, which takes into account the soil-adsorbed urea. Different values of the urea diffusion coefficient (D_{urea}), a floodwater depth of 2 cm, and a volumetric water content of 0.5 were incorporated into the model equations. The best fit of the measured vs. calculated data occurred with a D_{urea} value of $3.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ with a regression coefficient of 0.95 and R^2 of 0.96. Figure 5 compares measured urea-N solution concentrations with values generated by the model

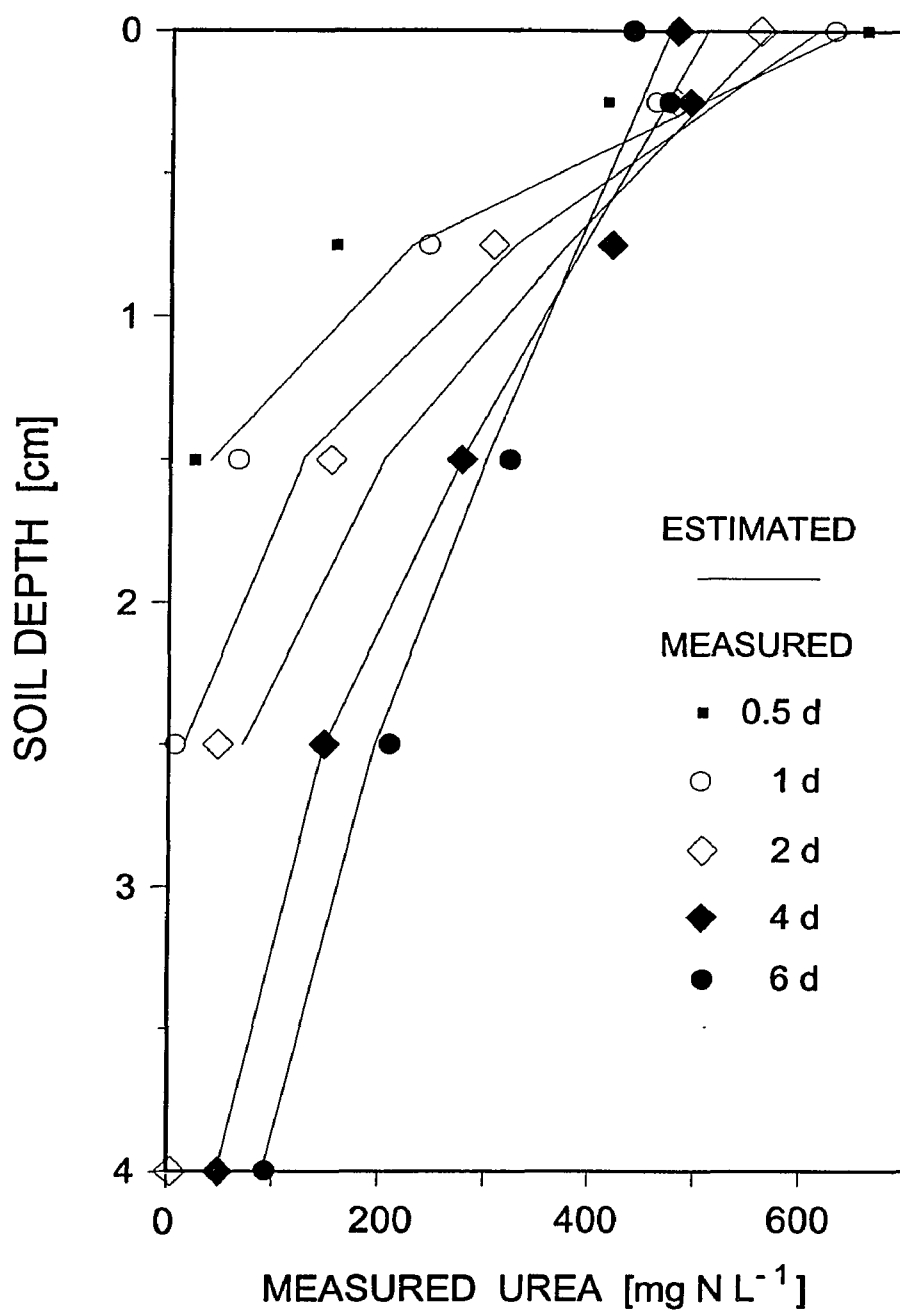


Fig. 5. Distribution of measured and modeled urea in autoclaved Crowley silt loam columns during 6 d. Points are experimental observations, lines are based on model output.

across the five sampling times and six soil column depths, using a D_{urea} of $3.5 \times 10^{10} \text{ m}^2 \text{ s}^{-1}$.

Urea hydrolysis rates in the soil and floodwater were estimated from nonsterilized soil columns and a combined urea diffusion-hydrolysis model. The rate of disappearance of urea followed first-order kinetics and rate constants (K_{rea}) were variable and increased with incubation time (Bouldin et al., 1991). The rate constants consistent with the data are presented in Table 2. Regression analysis of the measured vs. calculated hydrolysis (variable rates) showed good agreement with a R^2 of 0.98. Value of K_{rea} in the soil ranged from 0.036 to 0.288 h^{-1} and estimated K_{rea} constants in the overlying water were much lower (0.00072-0.0144 h^{-1}).

A search of the literature revealed that little has been published on urea movement and subsequent transformations in flooded soil profiles. Most of the published work was conducted under unsaturated aerobic soil conditions. In a recent study, Sadeghi et al. (1989) examined urea diffusion in seven unsaturated soils with varying properties. Following urea application (200 kg N ha^{-1}) to the soil surface, urea diffusion coefficients (D_s) were estimated by sectioning the soil cores 48 h after N addition. Diffusion coefficients in the seven soils varied from 0.87 to $8.05 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and the authors noted that the D_s values were very sensitive to soil water content. The higher D_{urea} values measured in our study would be expected because of saturated conditions and an overlying floodwater layer. In a modeling study, Rachhpal-Singh and Nye (1984) calculated a urea diffusion coefficient of $1.38 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ after urea was applied (210 kg N ha^{-1}) to unsaturated sandy loam soil cores.

Yadav et al. (1987) investigated the effects of temperature and moisture on urea hydrolysis in two high-pH soils (sandy and clay loams) and concluded that urea hydrolysis followed first-order reaction kinetics during a 12-h incubation period. The urea-hydrolysis rate constants (K) increased in both soils with increasing moisture content (20% FC to FC) and ranged from 0.019 to 0.044 h⁻¹ for the sandy loam soil and 0.049 to 0.095 h⁻¹ for the clay loam. Rate constants decreased when a 2-cm layer of standing water was established over the soil surface (0.023 for the sandy loam and 0.078 for the clay loam). Their values of K were similar to the urea hydrolysis rate at 0- to 12-h (0.036 h⁻¹) in this experiment. But the rate constant in this study increased to 0.216 and 0.288 h⁻¹ for the 12- to 24- and 24- to 48-h time intervals, respectively. Lindau et al. (1989) measured urea hydrolysis in one calcareous and three acid rice soil suspensions under oxidizing and reducing conditions after an initial urea application of 50 $\mu\text{g N g}^{-1}$ soil. Rate constants (K) in the oxidized acid soil suspensions were higher and ranged from 0.054 to 0.094 h⁻¹ compared with reduced suspensions (0.028 to 0.062 h⁻¹). Values of K for the calcareous oxidized and reduced soil suspensions were much higher (0.369 and 0.403 h⁻¹, respectively). Vlek and Carter (1983) investigated the effect of soil environment on the rate of urea hydrolysis and showed that hydrolysis could be described by zero- or first-order equations, depending on soil conditions and method of urea application. Vlek and Carter (1983) also noted that application of prilled urea to the soil caused a lag phase in initiation of hydrolysis, followed by first-order kinetics; then the rate of hydrolysis increased rapidly. The results and the variables urea-hydrolysis rates in urea diffusion plus hydrolysis columns

would also indicate that a lag phase existed under flooded conditions when urea was dissolved and mixed into the floodwater. The lag time was probably due to the diffusion of urea from the floodwater layer into the soil profile.

This study shows that urea adsorption by the soil was small but increased at the concentration of added solution urea-N increased. Urea-hydrolysis rates were variable and increased with incubation time and followed first-order reaction kinetics. The data generated in these experiments provide a basis from which urea behavior in flooded soils can be modeled. Such models may be helpful in selecting management practices that will improve N-fertilizer use efficiency in flooded rice.

Laboratory studies do not necessarily reflect actual flooded rice field conditions. Additional research is needed on urea movement and transformations under varying fields conditions. In addition, the presence of rice plants and algae may greatly influence urea-N behavior in flooded soils. In any event, the rate of urea hydrolysis in both soil and floodwater should be measured under field conditions.

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CHAPTER II

DISTRIBUTION OF AMMONIUM AND NITRATE IN FLOODED SOIL COLUMNS AFTER UREA APPLICATION UNDER AEROBIC AND ANAEROBIC CONDITIONS

Introduction

Ammonium formed from urea hydrolysis in flooded rice soils is considered to be the major N component which plays an important role in N availability to the rice plant. High concentrations of NH_4^+ -N concomitant with increasing floodwater pH, after urea hydrolysis, may lead to the high loss of NH_3 via volatilization (Kissel et al., 1988, Van Diest, 1991). However, at lower rates of urea application or under conditions that are not favorable for NH_3 volatilization, high concentrations of NH_4^+ may diffuse into the soil, where it is rapidly adsorbed onto the cation exchange complex of the soil (Patrick et al., 1985). Urea diffusion into the soil before hydrolysis is another factor that affects the pattern of NH_4^+ distribution in soil. In the previous study using Crowley silt loam soil, it was found that urea has a high potential to diffuse to the soil layer of 7.5- to 10-cm in 4 d if urea hydrolysis was inhibited. If hydrolysis does occur, however, urea was never found in soil layers lower than 2 cm and all of the applied urea in the soil columns was hydrolyzed within 4 d (Hongprayoon et al., 1991). In reduced soils, that have large amounts of Fe^{++} and Mn^{++} adsorbed on the exchange

complex, a larger percentage of NH_4^+ will be present in the soil solution which makes it more easily to move down the soil profile. Some NH_4^+ may be immobilized into microbial tissue or fixed by clay minerals resulting in lower concentration of NH_4^+ moving deeper into soil layers. The fixation rate of NH_4^+ is relatively rapid, determined mainly by ion diffusion. The magnitude of NH_4^+ fixation varies but depends mostly on clay type (Kai and Wada, 1979). Usually less than 10% of the added NH_4^+ undergoes fixation (Patrick et al., 1985)

Oxidized-reduced layers of the soil is another factor that influences the transformation of NH_4^+ from urea. Reddy et al. (1976) reported the formation of oxidized-reduced soil layers in Crowley silt loam soil and the thickness of the aerobic layer was about 0.5 and 1.25 cm after 15 and 30 days of flooding, respectively. The oxidized layer of the soil surface, formed from O_2 diffusion through the floodwater, promotes the nitrification process where NH_4^+ is oxidized to NO_3^- . Nitrate can readily diffuse or leach into the underlying anaerobic layer where it can be denitrified.

The objective of this study was to investigate the distribution of NH_4^+ - and NO_3^- -N in flooded soil columns under aerobic and anaerobic conditions after urea addition.

Materials and Methods

Ammonium adsorption

Forty g of autoclaved Crowley silt loam soil (autoclaved at 120°C, 15 psi for 2 h) was equilibrated with 20 ml of sterilized deionized water containing NH_4Cl at increasing concentrations of 0, 100, 200, 399, 600, 800, 999, and 1200 mg N L^{-1} . Each treatment was duplicated and incubated at 30 °C for 48 h. Soil suspensions were then vacuum filtered (Whatman no.42). Filtrates were collected and the soils were leached with 400 ml of isopropyl alcohol to eliminate soil solution NH_4^+ . Leached soils were extracted by shaking with 2 M KCl for 1 h. The NH_4^+ content in the soil solutions and adsorbed NH_4^+ in the KCl extracts were determined by steam-distillation procedures. Fixed NH_4^+ in the soil was estimated by subtracting the NH_4^+ in the soil solution and the adsorbed NH_4^+ in KCl extracts from total NH_4^+ added (Keeney and Nelson, 1982; O'Tool, 1991).

Ammonium and nitrate distribution

Forty-eight PVC columns (30-cm length by 7.73-cm i.d.) were packed with nonsterile Crowley silt loam soil. To study the distribution of NH_4^+ - and NO_3^- N under anaerobic conditions, twenty-four columns were sealed and N_2 was flushed through the soil columns to remove O_2 and prevent nitrification. Nitrogen-saturated water was added to the columns from the base until a 2-cm floodwater layer established. To study the distribution of NH_4^+ - and NO_3^- N under atmospheric O_2 , another twenty-four columns

were left open to the atmosphere. Distilled water was used to fill the soil columns until a 2-cm floodwater layer was formed. Both sets of columns were preincubated in the dark at 30 °C. After preincubation, the floodwater layer was removed from 12 anaerobic and 12 aerobic columns and replaced with a urea solution (N_2 purged for sealed columns) containing 750 mg N L^{-1} . Columns were then incubated in the dark for 0, 8, 15, and 30 d at 30 °C. At each sampling interval, three columns of each treatment and a control were removed from the incubator and sectioned into 10 layers (0.5, 1.0, 2.0, 3.0, 5.0, 7.5, 10.0, 12.5, 15.0, and 17.5 cm). Ammonium-N and NO_3^- -N were extracted from the soil sections with 2 M KCl under anaerobic (N_2 purged) and aerobic conditions. Floodwater was also collected from all columns. The NH_4^+ - and NO_3^- -N concentrations in the floodwater and in the KCl extracts were determined by steam-distillation procedures (Keeney and Nelson, 1982). The concentration of both NH_4^+ -N and NO_3^- -N was based on the soil moisture content.

Results and Discussion

Ammonium adsorption

The adsorption and fixation of NH_4^+ is shown in Table 7. It was found that adsorption of NH_4^+ by the soil ranged from 30.8 to 275.2 $\mu\text{g N g}^{-1}$ soil depending on concentration of added NH_4^+ . The amount of adsorbed NH_4^+ generally increased with increasing concentration of added NH_4^+ . Nevertheless, percentage of adsorption decreased when concentrations of added NH_4^+ increased (Figure 6). The percentage of adsorbed NH_4^+ decreased from 61.6% at the concentration of 100 mg N L^{-1} to 45.9% at 1200 mg N L^{-1} with an overall average of 51.8% adsorbed over the range of added NH_4^+ -N concentration. Similar trends were found in NH_4^+ fixation process that when concentration of the added NH_4^+ -N increased the total amount of fixed NH_4^+ also increased but the percentages of fixed NH_4^+ decreased. Fixation of NH_4^+ occurred at lower percentages than adsorption 23% was fixed at the concentration of 100 mg N L^{-1} and 16.7% was fixed at 1200 mg N L^{-1} (Figure 6). The simplified adsorption equation (de Hann and Zwerman, 1976; Rao and Ahmad, 1983) was applied to calculate the coefficient of NH_4^+ adsorption and fixation from data obtained in this study.

$$K = (x/m)/C$$

Where x/m = $\mu\text{g NH}_4^+$ -N adsorbed or fixed g^{-1} soil, C = equilibrium concentration of NH_4^+ -N in solution ($\mu\text{g NH}_4^+$ -N mL^{-1}), and K = adsorption or fixation coefficient. In

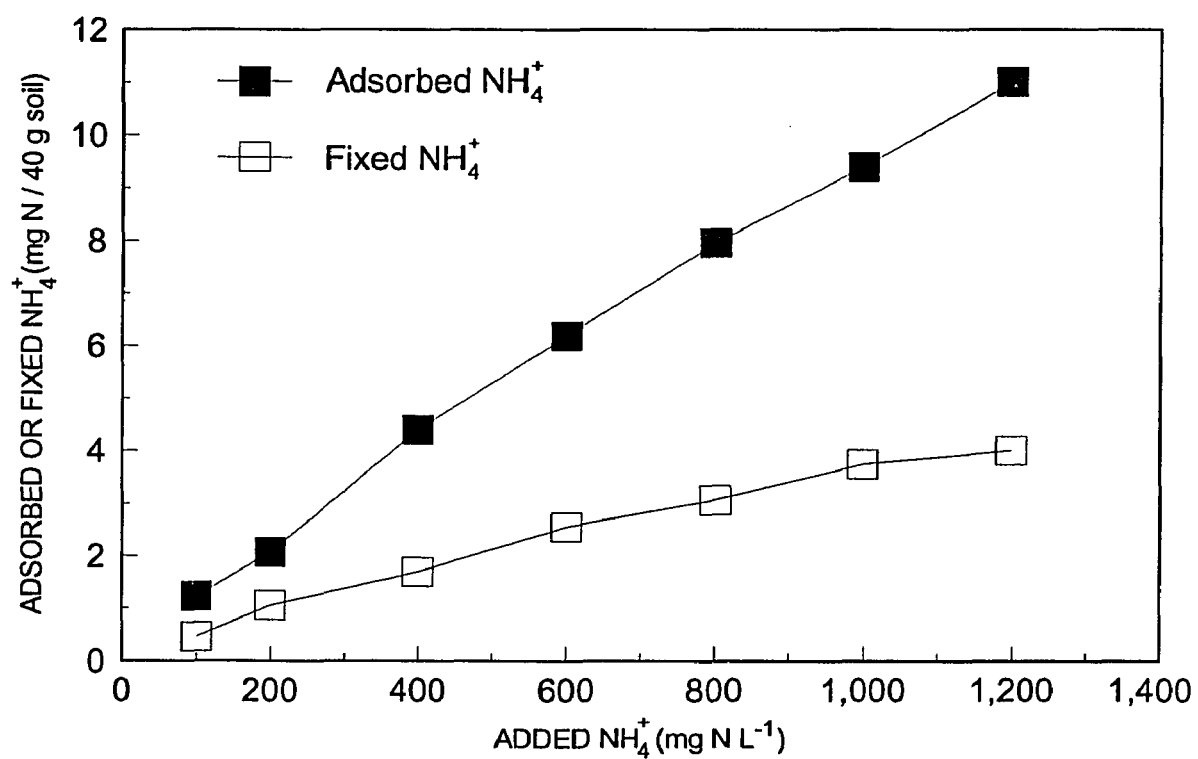


Fig. 6. Effect of ammonium concentration on ammonium adsorption and ammonium fixation in Crowley silt loam soil.

Table 7. Effect of ammonium solution concentration on the ammonium adsorption and ammonium fixation in Crowley silt loam soil.

Concentration of added NH_4^+ mg N L^{-1}	NH_4^+ in soil solution mg N L^{-1}	Adsorbed NH_4^+ $\mu\text{g N g}^{-1}\text{soil}$	Fixed NH_4^+ $\mu\text{g N g}^{-1}\text{soil}$	NH_4^+ adsorption coefficient	NH_4^+ fixation coefficient
100	15.6	30.8	11.5	1.98	0.74
200	43.3	51.8	26.6	1.20	0.61
399	95.6	109.7	42.4	1.15	0.44
600	163.5	154.5	63.7	0.95	0.39
800	248.9	199.0	76.6	0.80	0.31
999	341.9	235.1	93.5	0.69	0.27
1200	449.2	275.2	100.0	0.61	0.22

this study the value K is defined as the ratio between adsorbed NH_4^+ or fixed NH_4^+ on soil ($\mu\text{g N g}^{-1}$ soil) and the NH_4^+ concentration in equilibrium concentration. Figure 7 shows logarithmic plots of x/m against $\log C$. Regression analysis of the $\log x/m$ vs $\log C$ showed good agreement with a R^2 of 0.99 in both NH_4^+ adsorption and NH_4^+ fixation. Coefficients of NH_4^+ adsorption and NH_4^+ fixation were shown in Table 7. Both values of coefficients decreased with increasing concentration of added NH_4^+ , with the average values of about 1.05 and 0.43 for NH_4^+ adsorption and NH_4^+ fixation, respectively. The amount of adsorbed and fixed NH_4^+ is relatively high compared to total NH_4^+ added and should have a major effect on movement of NH_4^+ in the soil. Broadbent and Tusneem (1971) measured NH_4^+ fixation in a waterlogged Sacramento clay and reported about 45% of the applied $(\text{NH}_4)_2\text{SO}_4$ was fixed but only negligible amounts were fixed in Maahas and Louisiana clays. The amount of fixed NH_4^+ in this experiment is relatively high even though it is lower than in the Sacramento soil. This fraction of NH_4^+ is considered not available for movement in soil, but it may be available to plants or microorganisms. The availability of fixed NH_4^+ is low and the magnitude depends on various factors in the soil (Kai and Wada, 1979, Mengel et al., 1990). High adsorption and fixation of NH_4^+ in Crowley silt loam soil may also influenced NH_3 volatilization to some extent since sorption of NH_4^+ by the soil will decrease the NH_4^+ concentration in the floodwater. Katyal and Gadalla (1990) reported that as CEC increased in five soils, NH_3 volatilization decreased.

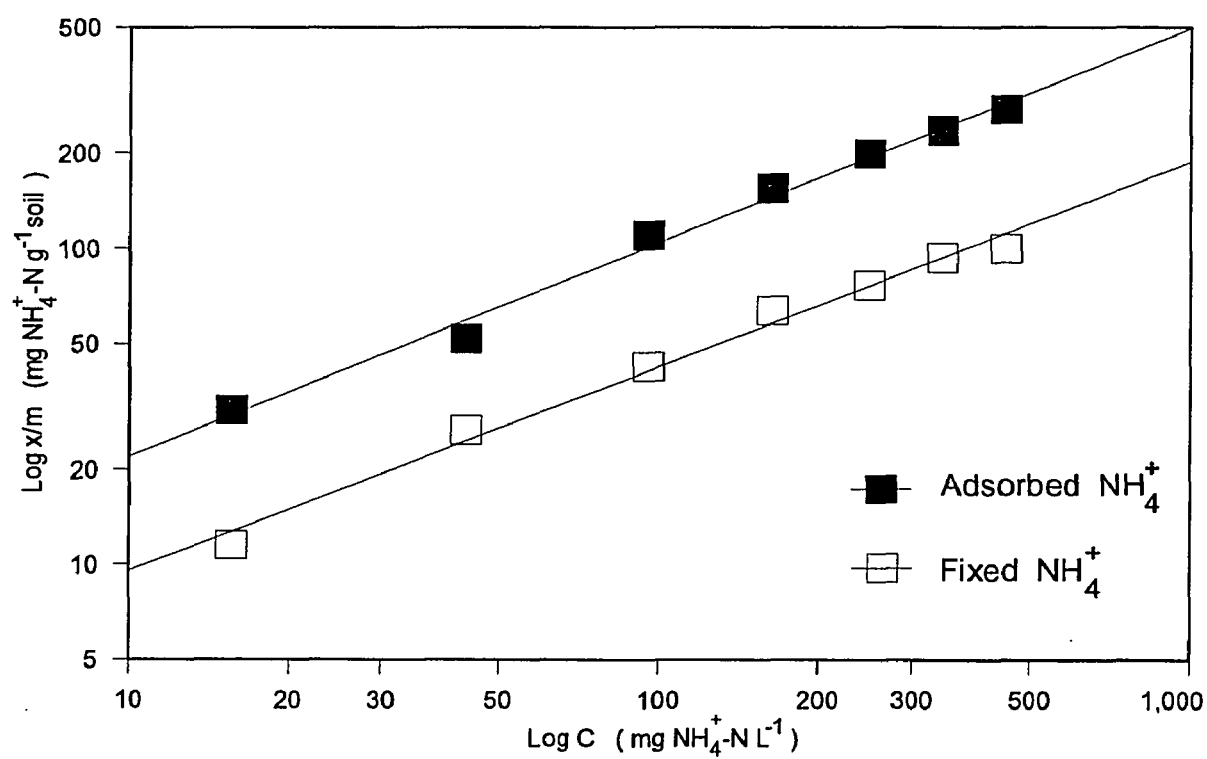


Fig. 7. Isothermal equilibrium adsorption and fixation of $\text{NH}_4^+\text{-N}$ by Crowley silt loam soil.

Distribution of ammonium and nitrate

The distributions of NH_4^+ under aerobic and anaerobic conditions are shown in Figures 8 and 9. Each point represents a mean of three values minus the average NH_4^+ -N concentration of control columns at 0, 8, 15, and 30 d after urea addition to the floodwater. After 4 d of incubation, under atmospheric O_2 conditions, all the urea in the soil columns was hydrolyzed and the highest concentration ($1374.1 \text{ mg N L}^{-1}$) of NH_4^+ was found in the 0- to 0.5-cm soil layer (data not shown). The level of NH_4^+ concentration in the floodwater was always lower than the NH_4^+ -N in the underlying soil layer. This is because most of applied urea was hydrolysed at the soil-water interface or after urea diffused into the soil where a high percentage of NH_4^+ can be adsorbed by the soil (Table 7). Incubation under aerobic or anaerobic conditions did not develop different patterns of NH_4^+ -N distribution. The average total NH_4^+ -N soil-column content (minus control values) of the atmospheric O_2 incubated columns was 59.4, 61.0, and 58.6 mg N at 8, 15, and 30 d after urea addition, respectively (Table 8). In the anaerobic incubated columns, the average total NH_4^+ - or NO_3^- -N column content did not significantly differ from the aerobic incubated columns. The average total NH_4^+ -N column content at 8, 15, and 30 d of the anaerobic incubated columns was 63.0, 61.4, and 65.3 mg, respectively (Table 9). The lower NH_4^+ -N plus NO_3^- -N values of both treatments compared to the total added urea-N reflects N assimilation, NH_4^+ sorption, NH_3 volatilization, or denitrification. The content and distribution of NO_3^- -N under both aerobic and anaerobic conditions, however, was relatively low.

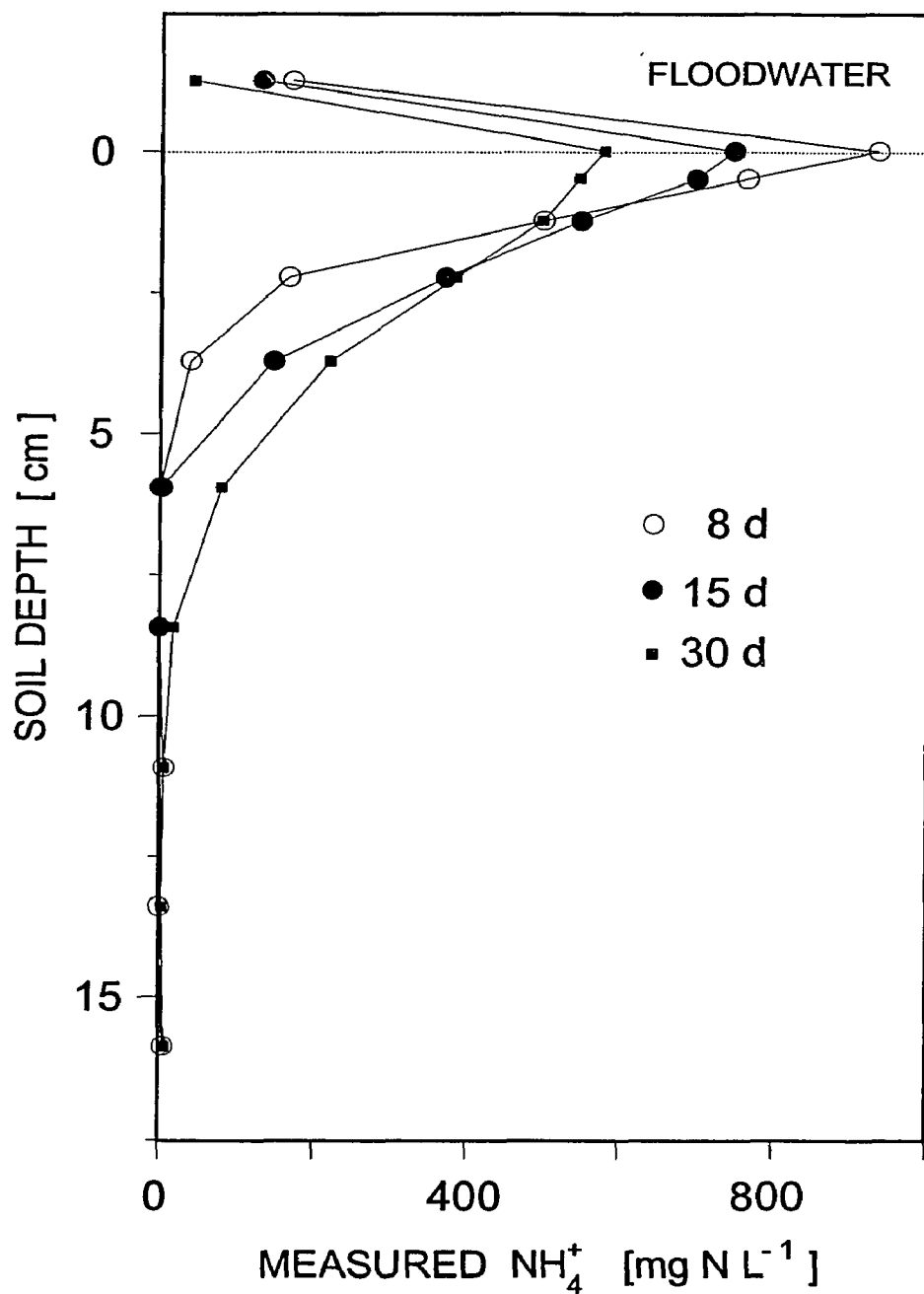


Fig. 8. Distribution of NH_4^+ -N in flooded Crowley silt loam soil columns incubated under aerobic conditions for 30 d after urea application.

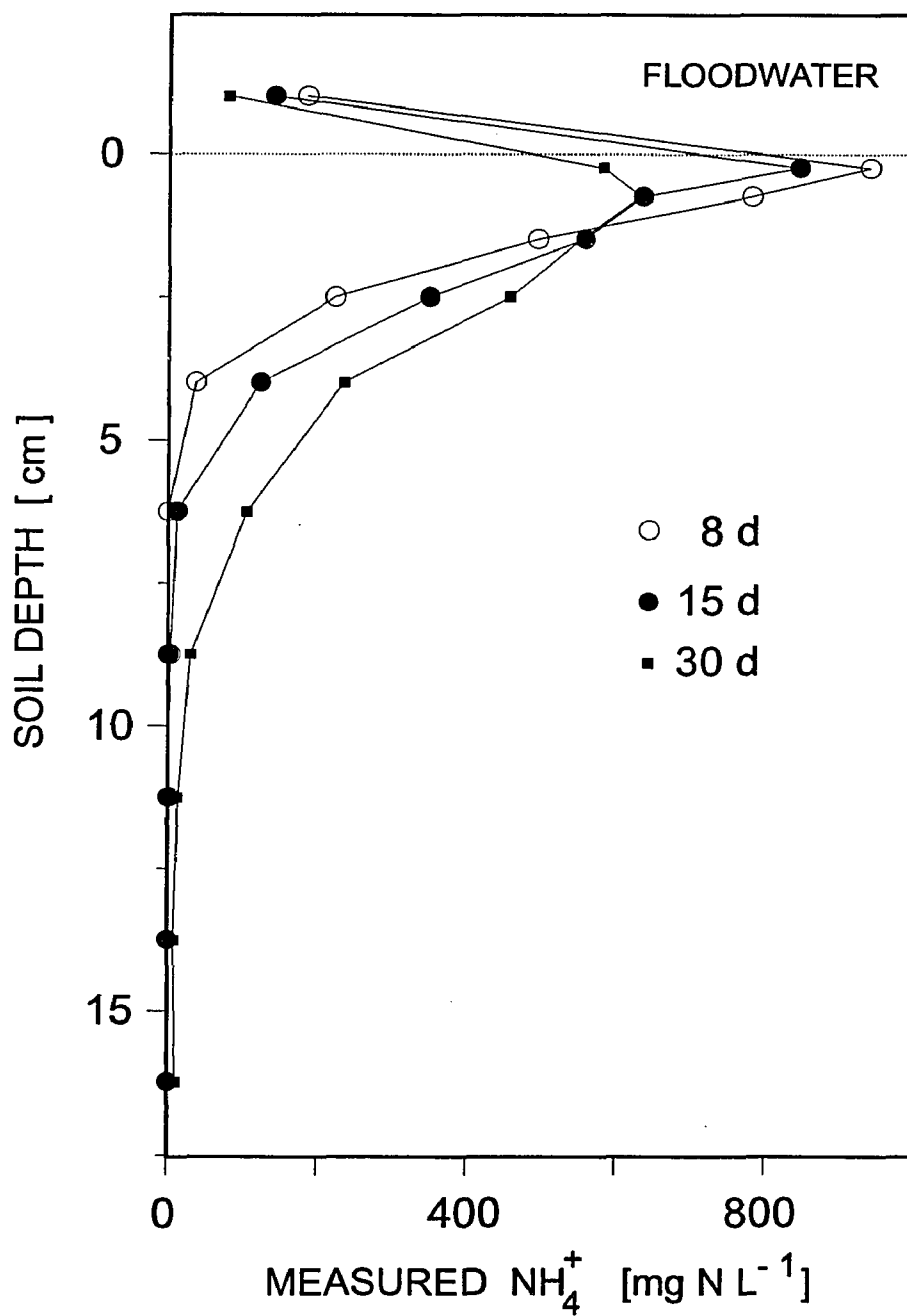


Fig. 9. Distribution of NH_4^+ -N in flooded Crowley silt loam soil columns incubated under anaerobic conditions for 30 d after urea application.

Table 8. Distribution of NH_4^+ -N and NO_3^- -N in flooded soil columns incubated under aerobic conditions during 30 d after initial urea application.

layer (cm)	NH_4^+ -N content (mg N)			NO_3^- -N content (mg N)		
	8 d	15 d	30 d	8 d	15 d	30 d
floodwater	14.32	11.51	3.68	0.07	0.00	0.00
0 - 0.5	17.26	12.24	10.94	0.20	0.04	0.07
0.5 - 1	9.26	8.79	6.94	0.14	0.05	0.08
1 - 2	11.96	13.09	11.91	0.21	0.08	0.13
2 - 3	4.04	8.67	8.80	0.19	0.00	0.15
3 - 5	1.78	6.58	9.84	0.19	0.14	0.25
5 - 7.5	0.00	0.17	4.08	0.51	0.07	0.49
7.5 - 10	0.00	0.00	0.85	0.00	0.34	0.20
10 - 12.5	0.35	0.00	0.19	0.00	0.19	0.12
12.5 - 15	0.00	0.00	0.04	0.17	0.00	0.12
15 - 17.5	0.42	0.00	1.30	0.00	0.02	0.14
TOTAL	59.38	61.04	58.57	1.69	0.94	1.63

Table 9. Distribution of NH_4^+ -N and NO_3^- -N in flooded soil columns incubated under anaerobic conditions during 30 d after initial urea application.

layer (cm)	NH_4^+ -N content (mg N)			NO_3^- -N content (mg N)		
	8 d	15 d	30 d	8 d	15 d	30 d
floodwater	15.26	12.11	5.76	0.09	0.41	0.00
0 - 0.5	18.93	12.87	7.56	0.10	0.07	0.14
0.5 - 1	9.83	8.34	7.61	0.00	0.00	0.00
1 - 2	11.63	13.28	12.53	0.12	0.09	0.06
2 - 3	5.25	8.31	9.55	0.00	0.05	0.00
3 - 5	1.59	5.50	12.05	0.14	0.05	0.00
5 - 7.5	0.00	0.73	5.23	0.18	0.00	0.00
7.5 - 10	0.11	0.03	1.30	0.00	0.00	0.00
10 - 12.5	0.39	0.00	0.70	0.00	0.00	0.00
12.5 - 15	0.00	0.00	0.63	0.12	0.00	0.00
15 - 17.5	0.00	0.22	2.38	0.00	0.00	0.00
TOTAL	63.00	61.39	65.31	0.76	0.67	0.20

In accordance with the small loss of N from the system and low level of NO_3^- -N, it may be concluded that the nitrification rate was very low in this experiment.

The NH_4^+ -N diffusion coefficient in the solution phase of the flooded soil columns and NH_4^+ sorption by the soil was estimated using the finite-difference equations described by Bouldin et al. (1991). The NH_4^+ diffusion coefficient and NH_4^+ sorption were varied in the model until the best fit ($R^2 = 0.92$) between measured and calculated NH_4^+ -N concentration was achieved (Boudin et al., 1991). The model produced best-fit estimates of $3.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for the diffusion coefficient and 2.0 for NH_4^+ sorption.

Reddy et al. (1980) measured the rate of NH_4^+ diffusion in three soils under flooded conditions using diffusion cells. Ammonium-N was added at a rate of $200 \mu\text{g N g}^{-1}$ soil and the cores were sectioned during the next 60 d. Calculated NH_4^+ diffusion coefficients ranged from 1.6 to $6.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Rachhpal-Singh and Nye (1984) measured NH_4^+ diffusion after urea was surface applied to unsaturated soil columns and estimated that the diffusion coefficient to be $1.9 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Comparison of diffusion coefficients for NH_4^+ -N calculated in this study with cited literature is difficult. The wide range of experimental conditions, soil types, and basis of calculation will only allow generalized comparison of results.

The concentration profiles of NH_4^+ -N from applied urea did not show different patterns between columns incubated under aerobic and anaerobic conditions. The results may reflect the low level of nitrification under these experimental conditions. The adsorption experiment showed that the sorption of NH_4^+ -N in the Crowley silt

loam soil was relatively high which may have a major effect on the rate of NH_4^+ -N movement in the soil. Under zero percolation in this experiment, most of the N from the applied urea was found to accumulated only in the top 10 cm from the soil surface during 30 d after urea application. The short distance translocation of NH_4^+ -N may reveal the effect of sorption of NH_4^+ -N onto the soil. Nevertheless, the movement of N from applied urea in the field may be influenced by other factors, especially percolating water which may leach N into the deeper soil layers. Additional research will be helpful for more understanding about N movement from applied urea.

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CHAPTER III

EFFECTS OF PERCOLATION RATES AND UREASE INHIBITOR ON DISTRIBUTION OF N FROM APPLIED UREA IN FLOODED SOIL COLUMNS

Introduction

Urea is the most popular N fertilizer in rice growing countries because of its high N content, low cost, and availability. However, it is not the ideal N fertilizer since the recovery by rice is low even with the best agronomic practices and controlled conditions. Most of the nitrogen-use experiments have found that the plant recovery is in the range of 20 to 40% of applied urea fertilizer (Craswell and Vlek, 1979; De Datta et al., 1988). Low N recovery of applied urea may be caused by many N loss pathways of including NH_3 volatilization, denitrification, leaching, ammonium fixation, and immobilization (De Datta, 1978). To improve efficiency of urea-N uptake by rice, it is imperative to understand the transformations and distribution of urea and its hydrolysis products in flooded soils and to develop management practices to minimize losses of N from this fertilizer.

In most lowland conditions, the root zone of rice occupies the top 25 to 30 cm of soil, and about 80% of the roots are concentrated in the top 7.5-cm soil layer (Ghildyal, 1978; Wickham and Singh, 1978). Distribution of N from applied urea in this zone is required to maximize the efficiency of fertilizer utilization. The movement

of water through the soil, however, can greatly affect the distribution of urea, NH_4^+ , and NO_3^- and may leach the nutrients from the root zone. The effect of percolation on losses of nutrients was estimated by Sherma et al. (1989) and a percolation rate of 10 mm d^{-1} caused $79 \text{ kg NH}_4^+\text{-N ha}^{-1}$ to be leached from a flooded rice soil. Nitrate is the most readily available nutrient to be leached because of its negative charge. In contrast, NH_4^+ can be adsorbed on cation exchange complexes and fixed by clay colloids in soils. Under O_2 -deficient conditions, the mobility of NH_4^+ is increased because a larger fraction of NH_4^+ is in the pore water instead of being adsorbed onto the exchange complex. This effect is due to displacement of NH_4^+ from the exchange complex by other cations that are mobilized as a result of reduction processes (Reddy and Patrick, 1983). Urea is intermediate between NO_3^- and NH_4^+ in leaching susceptibility since it is partially adsorbed by the soil complex. Adsorption of urea was considered not to influence leaching over the long term because it is rapidly hydrolyzed in the soil after application (Rao, 1983). However, the present interest in using urease inhibitors to retard urea hydrolysis may increase the significance of urea adsorption on its movement in the soil.

Patterns of urea, NH_4^+ , and NO_3^- distribution and movement in the soil profile are complicated processes. Urea undergoes hydrolysis while moving downward and NH_4^+ concentrations in the soil increase as urea is hydrolyzed. In the oxidized soil layer, microorganisms can oxidize NH_4^+ to NO_3^- and the NO_3^- is readily leached. Adsorption of urea and NH_4^+ and NH_4^+ fixation can lead to an accumulation of both N forms in the upper soil layer (Rachhpal-Singh and Nye 1988; Rao, 1983). During

percolation, solutes move not only in response to solute concentration gradients, but also with the flow of water (Davidson et al. 1983). Transport of solutes can be affected by many factors other than reactivity of solutes. Coefficient of mechanical dispersion and molecular diffusion, soil water content, pore-water velocity, the diffusive transfer of solute between mobile and immobile regions of the liquid phase are factors that govern the mobility and distribution of solutes in soil (Davidson et al. 1983; Jaynes, 1991; Leij and Dane, 1989; Wagenet, 1983; Wierenga, 1977).

Volatilization of NH_3 from flooded soil is another major N loss mechanism. The amount of loss varies widely depending on soil parameters, environmental conditions, and management practices. Loss of urea-N through NH_3 volatilisation was reported by Ventura and Yoshida (1977) to be less than 10 % but De Datta et al. (1991) reported losses ranging from 46% to 54% during 8 d following urea application to flooded rice paddies. Several approaches have been taken to minimize NH_3 volatilization from urea. Modified urea forms such as S-coated urea, or isobutylidene urea were used to reduce the rate of urea hydrolysis, thereby preventing the accumulation of ammoniacal-N in the floodwater (Mikkelsen and De Datta, 1979 ; Voss, 1984). Urease inhibitors are another recent manufacturing technology developed to delay the hydrolysis of applied urea. A new urease inhibitor, N-(n-butyl)thiophosphoric triamide (NBPT), was found to be more effective than phenyl phosphorodiamidate (PPD) in retarding urea hydrolysis in aerobic moist soil (Bremner and Chai, 1986). Buresh et al. (1988) studied the effects of two urease inhibitor, PPD and NBPT, on rice growth and yield. Both urease inhibitors were found to increased

grain yield, but the yield increases were small. Lu et al. (1989) found NBPT to be more effective in retarding urea hydrolysis under oxidizing than reducing conditions and at 5 d after urea addition to soil suspensions, 57% of the added urea remained in the oxidized soils compared to only 4% under reducing soil conditions. Carmona et al. (1990) studied the effects of NBPT on NH_3 volatilization from urea applied on a wet soil (field capacity) and found the inhibitor reduced the NH_3 volatilization rate significantly. In addition to decreasing NH_3 volatilization, urease inhibition can affect the distribution of urea in the soil profiles. Cai et al. (1989) reported that addition of NBPT increased the retention of N from applied urea in flooded soils about 27% at 35 d after urea application but the effectiveness of NBPT varied markedly, depending on type of soils, cultural conditions and algal growth. The distribution of urea or the hydrolysis products in flooded soils may greatly affect the efficiency of N recovery by rice plants. Formation of NH_4^+ -N in the reduced soil layer is required to reduce N loss through the denitrification process (Patrick et al. 1985). Movement of urea or its hydrolysis products from the rice rhizosphere, however, may lead to more losses through leaching or NH_4 fixation in the soil layers below the root zone.

There is limited information on the effects of percolation and urease inhibitors on N distribution of applied urea in flooded soils. To develop proper management practices and to improve the effectiveness of urea utilization by flooded rice, a better understanding about urease inhibitions and the percolation process is required. The objectives of this study were 1) to determine the distribution of urea-N and its hydrolysis products under different rates of percolation and 2) investigate the effect of

the urease inhibitor, NBPT on distribution of urea and N forms from applied urea under different percolation rates.

Materials and Methods

Thirty-six PVC columns (30-cm length by 7.73-cm i.d.) with a 2-cm-thick paraffin-petroleum jelly base (4:1 ratio) were constructed and 1,130 g of Crowley silt loam soil was uniformly packed into each column (bulk density = 1.3 g cm^{-3}). Soil columns were slowly filled with water from the base until the columns were saturated and a 2-cm floodwater depth established. Columns were incubated in the dark at room temperature for 3 months to develop oxidized and reduced soil layers, before urea-N was added. During incubation, distilled water was added every week to maintain the floodwater level at a 2 cm depth. After the incubation, columns were moved into a 30°C incubator 7 d before urea addition. Twenty-four columns were set up as shown in Figure 10 to control water flow through the columns. Flow rates were controlled by a hosecock clamp at the drainage outlet. Half of the columns (12 columns) were set to have a percolation rate = 0.5 cm d^{-1} , another 12 columns were set at a percolation rate = 1.0 cm d^{-1} and additional 12 columns were used as controls (no percolation). To investigate the effect of percolation without urease inhibitor, floodwater of 6 columns of each percolation rate (including no percolation) was removed and replaced by 93.86 ml of urea solution (750 mg N L^{-1}). This volume of urea solution established a 2-cm layer of floodwater. The total N added in each column was 70.4 mg urea-N. The other 6 columns of each percolation rate were used to determine the effects of urease inhibitor had on urea-N transformations and dispersion in the soil columns. Floodwater of these columns was removed and substituted with 93.86 ml urea solution

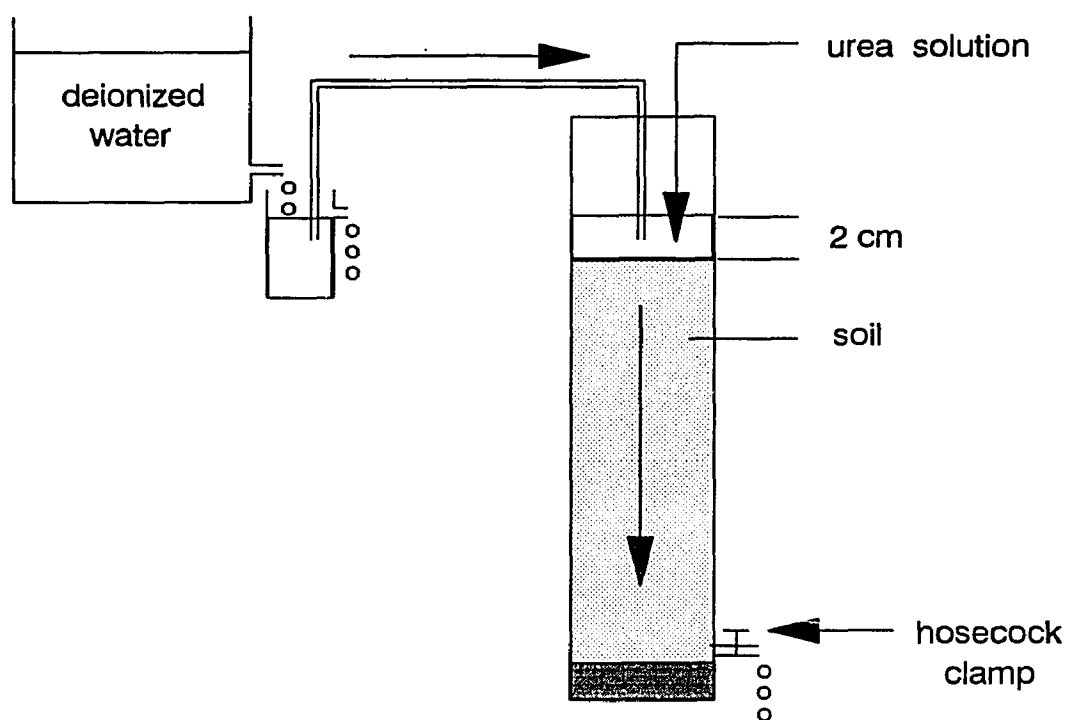


Fig. 10. Percolation apparatus for soil columns.

(750 mg N L⁻¹) containing the urease inhibitor, N-(n-butyl) thiophosphoric triamide (NBPT) at 10% of the weight of urea. After urea addition, all columns were incubated in the dark at 30°C for 0.5, 1 and 2 d. At the end at each incubation period, duplicate columns of each treatment were sampled. Floodwater was collected and each column was sectioned into eight soil layers at depth of 0.5, 1.0, 2.0, 3.0, 5.0, 7.5, 10, and 12.5 cm from the soil surface. Weights of floodwater and each soil section were recorded and the soil water content was determined (105°C). Urea was extracted from the soil sections by shaking for 1 h with 2 M KCl (1:10 soil:KCl ratio) containing 5 µg mL⁻¹ of phenylmercuric acetate (PMA). Soil solutions were filtered and the solution extracted was analyzed for urea-N content. Urea in the floodwater and soil-section extracts was determined colorimetrically (Bremner. 1982).

Results and Discussion

Effect of percolation rates on the distribution of N from applied urea.

The pattern of distribution of urea in soil columns with the zero percolation rate was compared with a previous experiment (Hongprayoon et al, 1991) in which the column incubation time was different from this experiment. In a previous experiment, columns were flooded for 3 d before urea addition, but columns in this experiment were flooded and incubated for 3 months before urea addition. The soil columns were incubated for 3 months to develop oxidized and reduced soil layers. The results showed no difference in the pattern of urea distribution at 0.5, 1, and 2 d. It appeared that the changes in soil physico-chemical and microbiological properties of the soil columns have little effect on urea distribution under zero percolation. Urea was rapidly hydrolyzed in the soil columns and 72.5% (Table 10) of the added urea was hydrolyzed within 2 d in this experiment compared to 78.6% in the earlier urea hydrolysis experiment (Table 6). Katyal and Gadalla (1990) observed a different result in a Guthrie silty clay loam where increasing presubmergence time, from 3 d to 14 d, increased the rate of urea hydrolysis. There was no obvious effect of incubation time on urea distribution in the Crowley silt loam soil which may have been due to the high rate of urea hydrolysis in this soil compared to the Guthrie silty clay loam.

The effects of percolation rates on the distribution of urea-N are shown in Figure 11(a-c) and Table 10. Urea hydrolysis appeared to required a lag period before the maximum rate of hydrolysis occurred. The average rates of disappearance of urea

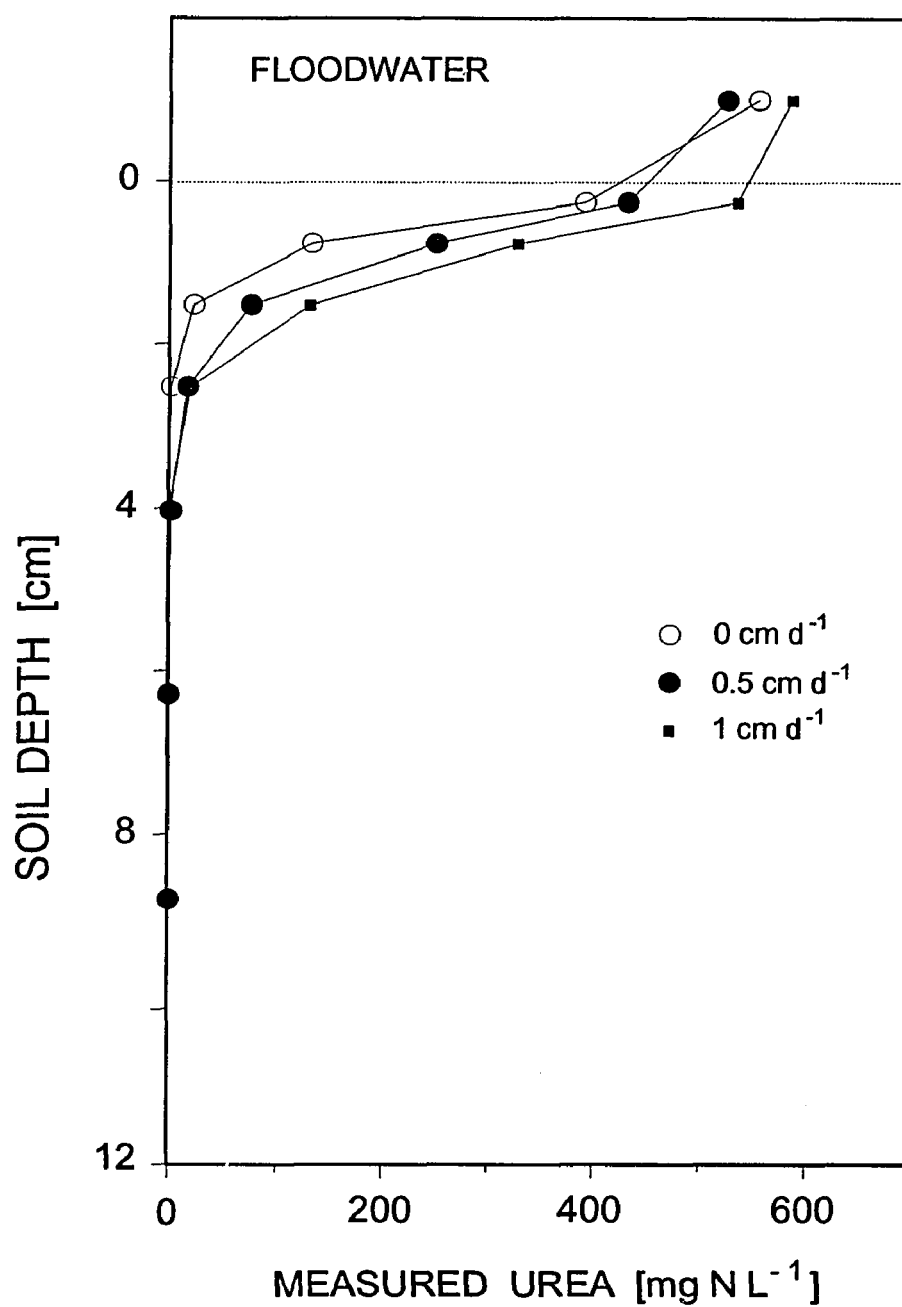


Fig. 11a. Effect of percolation rates on urea distribution in flooded Crowley silt loam soil columns incubated without urease inhibitor for 0.5 after urea application.

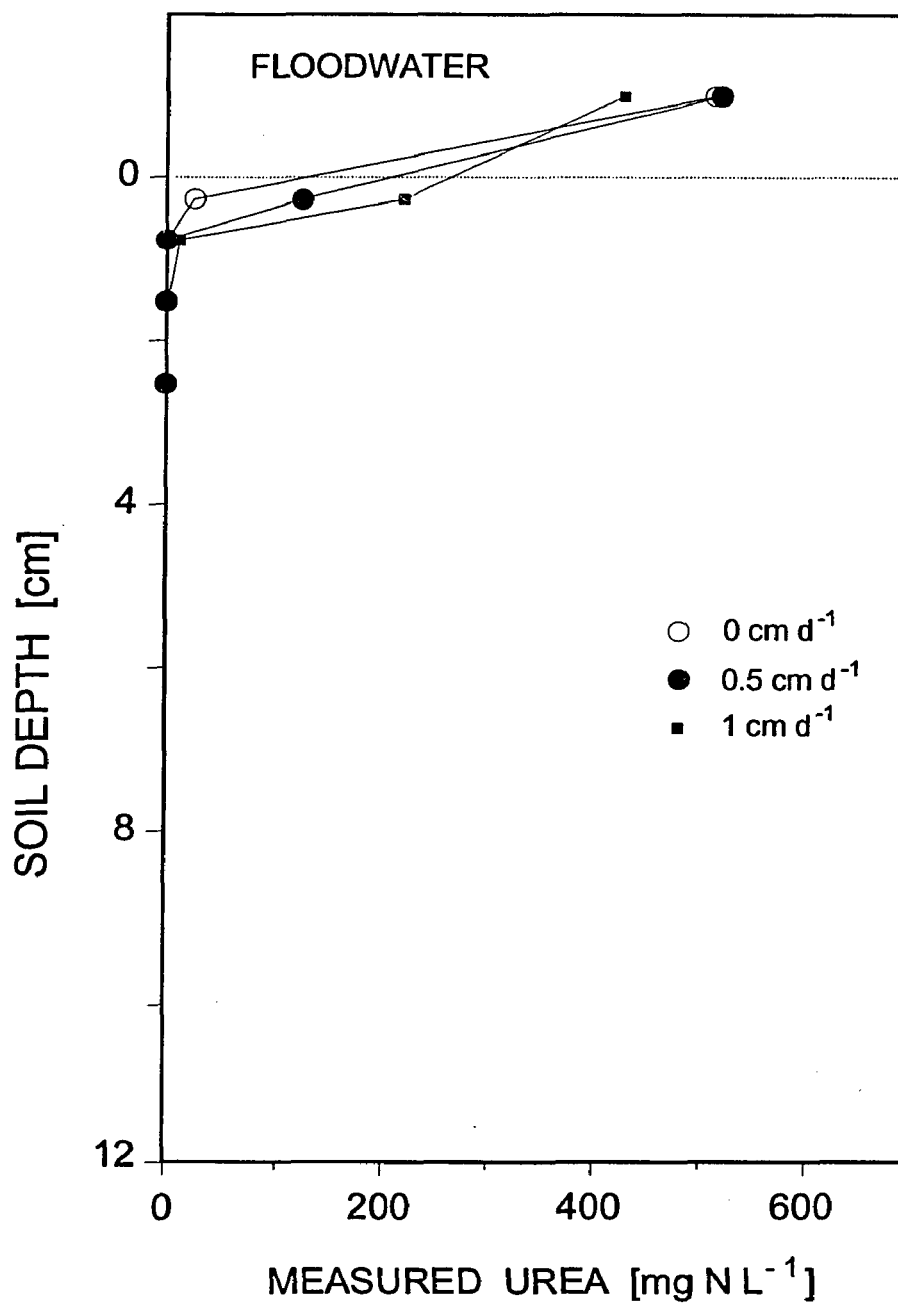


Fig. 11b. Effect of percolation rates on urea distribution in flooded Crowley silt loam soil columns incubated without urease inhibitor for 1 d after urea application.

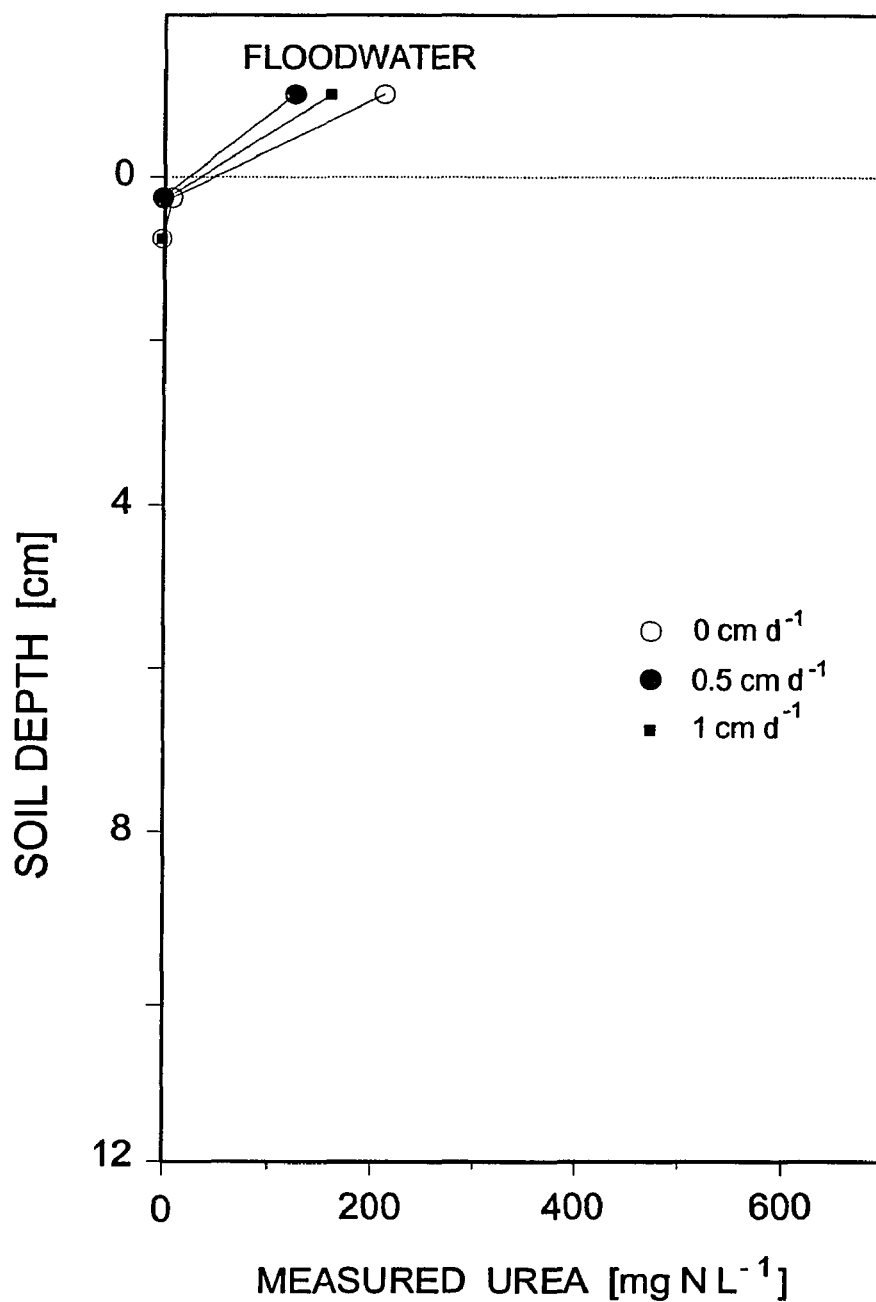


Fig. 11c. Effect of percolation rates on urea distribution in flooded Crowley silt loam soil columns incubated without urease inhibitor for 2 d after urea application.

Table 10. Effects of percolation rates on the distribution of urea-N, NH_4^+ -N, and NO_3^- -N in flooded Crowley silt loam soil columns incubated without NBPT during 2 d after urea application.

Incubation periods (days)	Layers (cm)	Percolation rates								
		0 cm d ⁻¹			0.5 cm d ⁻¹			1 cm d ⁻¹		
		UREA-N (mg-N)	NH_4^+ -N (mg-N)	NO_3^- -N (mg-N)	UREA-N (mg-N)	NH_4^+ -N (mg-N)	NO_3^- -N (mg-N)	UREA-N (mg-N)	NH_4^+ -N (mg-N)	NO_3^- -N (mg-N)
0.5	floodwater	52.42	0.95	0.82	54.53	0.59	0.40	48.69	0.32	0.09
	0-0.5	8.55	1.38	0.01	7.94	1.76	0.15	11.65	1.99	0.12
	0.5-1	1.71	0.12	0.00	3.09	0.38	0.00	4.00	0.24	0.03
	1-2	0.55	0.16	0.07	1.79	0.43	0.00	3.03	0.17	0.00
	2-3	0.03	0.00	0.00	0.44	0.00	0.00	0.46	0.00	0.00
	3-5	0.00	0.00	0.00	0.08	0.00	0.00	0.00	0.00	0.00
	5-7.5	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
	7.5-10	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.00
	10-12.5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	TOTAL	63.27	2.61	0.90	67.88	3.16	0.61	67.83	2.72	0.25
1	floodwater	48.97	1.79	0.35	45.54	1.48	0.28	47.59	1.23	0.25
	0-0.5	0.56	13.97	0.00	2.40	11.16	0.06	4.47	5.48	0.02
	0.5-1	0.00	4.27	0.00	0.01	5.78	0.02	0.16	5.21	0.00
	1-2	0.00	1.48	0.00	0.01	5.08	0.02	0.03	5.94	0.00
	2-3	0.00	0.33	0.00	0.00	1.32	0.00	0.00	2.86	0.00
	3-5	0.00	0.02	0.15	0.00	0.15	0.00	0.00	2.58	0.00
	5-7.5	0.00	0.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	7.5-10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	10-12.5	0.00	0.09	0.00	0.00	0.44	0.00	0.00	0.00	0.00
	TOTAL	49.53	22.25	0.50	47.96	25.42	0.39	52.25	23.30	0.27
2	floodwater	19.13	8.91	0.16	10.68	6.98	0.11	14.11	10.05	0.09
	0-0.5	0.21	22.17	0.17	0.00	23.28	0.00	0.10	14.08	0.00
	0.5-1	0.00	5.93	0.00	0.00	7.24	0.01	0.00	10.15	0.00
	1-2	0.00	3.89	0.06	0.00	7.42	0.00	0.00	14.67	0.00
	2-3	0.00	0.54	0.05	0.00	2.12	0.03	0.00	8.09	0.00
	3-5	0.00	0.00	0.00	0.00	0.56	0.00	0.00	3.87	0.00
	5-7.5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.00
	7.5-10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	10-12.5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	TOTAL	19.33	41.45	0.45	10.68	47.61	0.15	14.21	61.02	0.09

were found to be 4.1, 16.4, and 17.6 mg urea-N 12 h^{-1} at time interval of 0 to 12 h, 12 to 24 h, and 24 to 48 h, respectively. Occurrence of the lag phase was also reported by Vlek and Carter (1983) in a Crowley silt loam and other soils. Rate of urea hydrolysis in this soil was relatively high compared to other soils (Al-Kanani et al., 1991; Carmona et al, 1990).

A strong percolation effect on urea movement was observed in the first 0.5 d of incubation. At the highest rate of percolation, 19.14 mg of the floodwater urea-N (27.2% of applied urea) was translocated into the soil compared to 13.35 (19%) and 10.84 mg urea-N (15.4%) at rates of 0.5 and 0 cm d^{-1} , respectively. At 1 d of incubation, most of the diffused urea in the soil layers was hydrolyzed and only a small amount of the urea remained in the soil especially in the columns with no percolation where <1% of the applied urea remained. Patterns of urea distribution in the soil columns are given in Figures 11 a-c. The apparent effect of percolation rates was shown at 0.5 d of incubation (Figure 11a) in which the highest rate of percolation retained the highest concentration of urea-N in each layer. At 1 and 2 d, most of the urea in the soil was hydrolyzed and did not show any pattern of distribution.

The effects of percolation on NH_4^+ -N distribution in soil columns is shown in Figure 12(a-c) and Table 10. The distribution of NO_3^- -N, however, was not shown because formation of NO_3^- -N was very low in all columns and differences were not significant. Formation of NH_4^+ -N confirmed the pattern of urea hydrolysis where the more urea hydrolyzed in the soil the higher the NH_4^+ -N concentrations. Average amounts of NH_4^+ -N formed from urea hydrolysis at 0.5, 1, and 2 d were 2.8, 23.7,

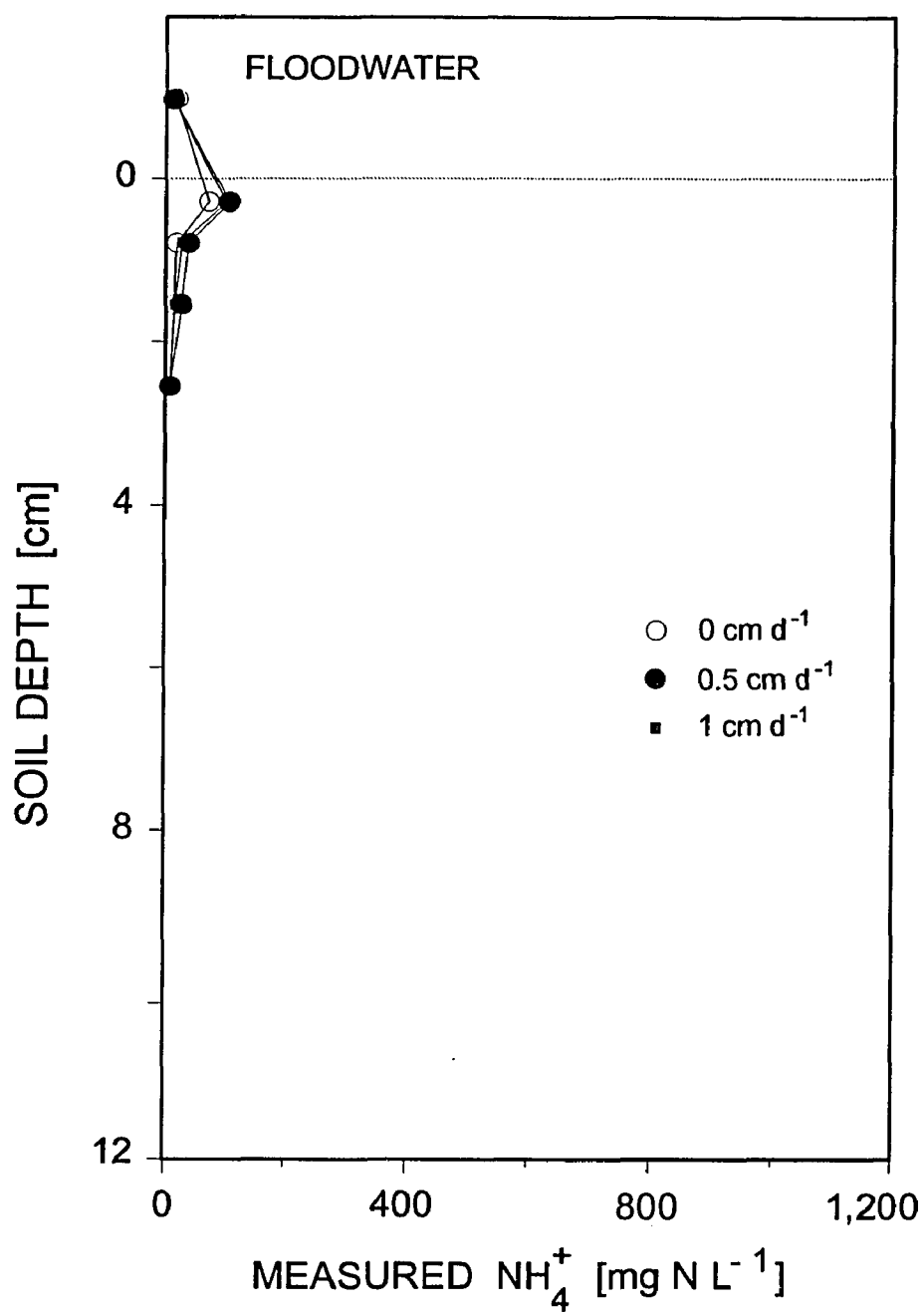


Fig. 12a. Effect of percolation rates on NH_4^+ -N distribution in flooded Crowley silt loam soil columns incubated without urease inhibitor for 0.5 d after urea application.

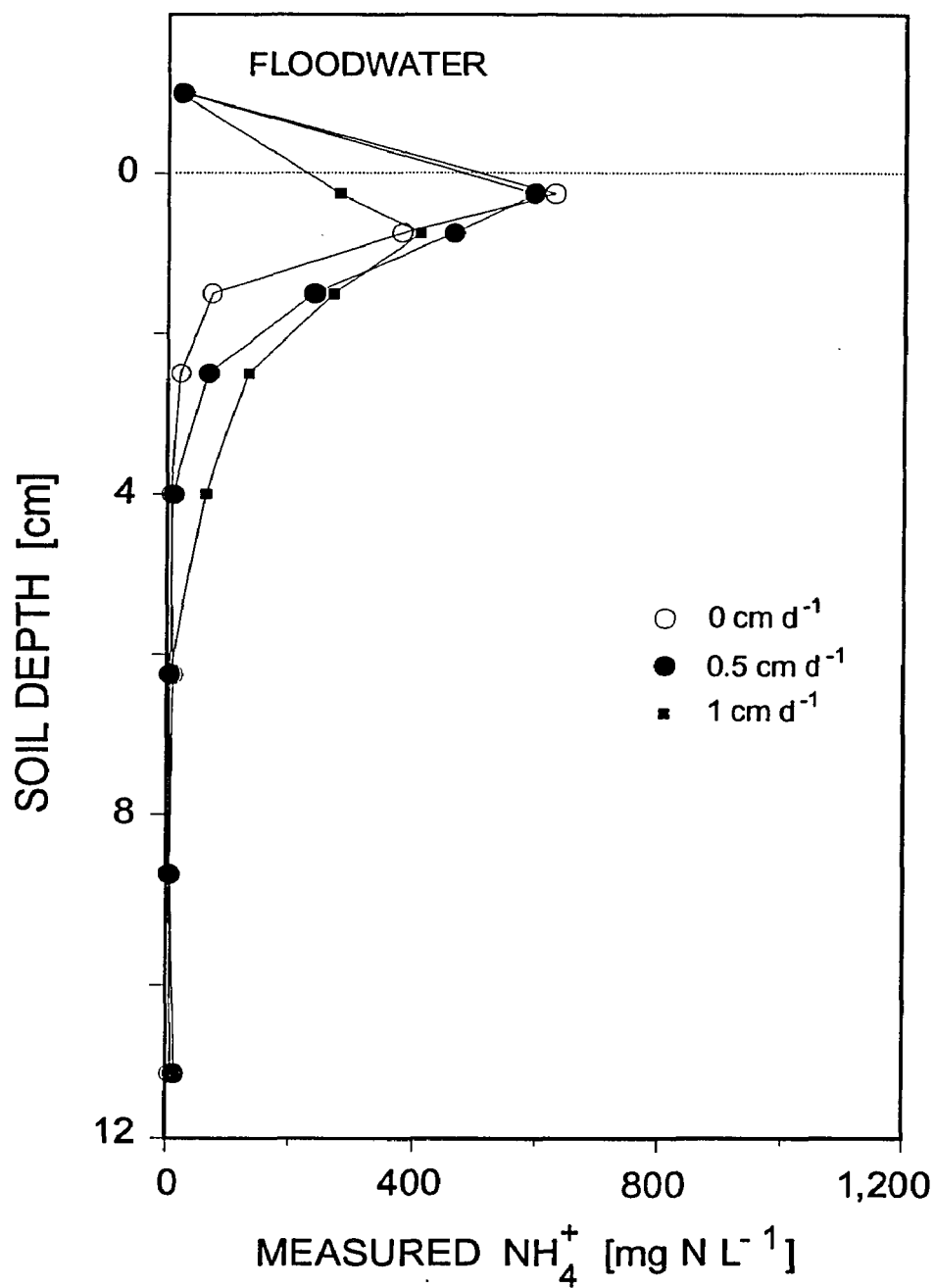


Fig. 12b. Effect of percolation rates on NH_4^+ -N distribution in flooded Crowley silt loam soil columns incubated without urease inhibitor for 1 d after urea application.

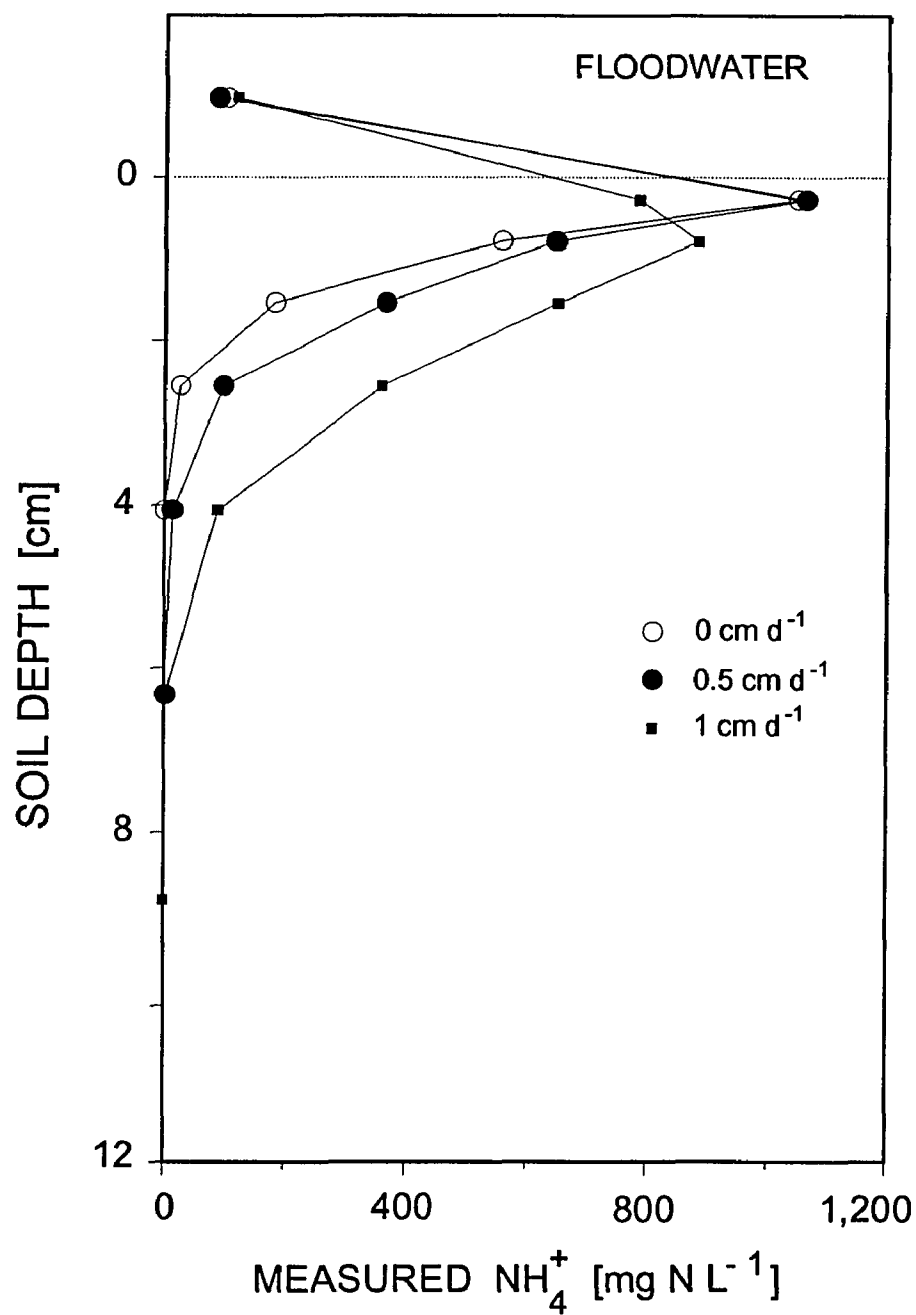


Fig. 12c. Effect of percolation rates on NH_4^+ -N distribution in flooded Crowley silt loam soil columns incubated without urease inhibitor for 2 d after urea application.

and 50.0 mg N column⁻¹, respectively. Since the average amount of urea disappearance from the columns was 4.1, 20.5, and 55.7 mg urea-N at 0.5, 1, and 2 d, respectively, the amount of NH₄⁺-N formed was found to vary directly with the amount of urea hydrolyzed. It was possible that some of the hydrolyzed urea-N may have been lost through other pathways especially NH₃ volatilization and some of the formed NH₄⁺-N may have been derived from organic matter decomposition or have been nitrified (Sharma et al., 1989). Percolation rates had little effect on NH₄⁺-N distribution compared to urea distribution. Only at 2 d of incubation did the highest rate of flow show a significant effect on movement of NH₄⁺-N. It was probable that the NH₄⁺ adsorption and NH₄⁺ fixation processes play a key role in reducing the mobility of NH₄⁺-N in soil. A preliminary study measuring adsorption and fixation of NH₄⁺ in a Crowley silt loam soil found that adsorption plus fixation ranged between 62.6 to 84.4% of applied NH₄⁺-N when the concentrations of applied NH₄⁺-N were between 100 to 1200 mg N L⁻¹. Although NH₄⁺-N was immobilized by the soil, it appeared that after 2 d, a large amount of NH₄⁺-N was translocated into the 2- to 3-cm, 3- to 5-cm, and 5- to 7.5-cm layers when the percolation rates were 0, 0.5, and 1 cm d⁻¹, respectively. This distribution of NH₄⁺-N may not only depend on the movement of NH₄⁺-N itself, but also on the movement of urea, which was less strongly retained by soil.

Effect of urease inhibitor (NBPT) on the distribution of N from applied urea under different percolation rates.

NBPT added in the floodwater with urea delayed hydrolysis of urea even after urea had diffused down into the lower soil layers. This showed the ability of NBPT to move along with urea and inhibit the activity of urease in the soil. The distribution of urea at 0.5 d (Figure 13a), when the hydrolysis rate was low, exhibited the same patterns as soil columns without the urease inhibitor (Figure 11a). The beneficial effect of the urease inhibitor in preventing urea hydrolysis was seen at 1 d and 2 d of incubation. A large concentration of urea was not hydrolyzed and translocated to the lower soil layers in the presence of NBPT. An average of 94.5 and 66.2% of applied urea (Table 11) remained in the soil columns after 1 and 2 d, respectively, compared to 70.9% after 1 d, and 20.9% after 2 d in columns without NBPT (Table 10). Percentage inhibition of NBPT on urea hydrolysis at 2 d was calculated from $(C-T)/C \times 100$, where T = amount of urea hydrolyzed in columns treated with NBPT, and C = amount of urea hydrolyzed in columns without NBPT (Bremner and Chai, 1986). Average percentage inhibition was 81.5% at 1 d and 56.7% at 2 d after urea application which were high compared to values reported by Cai et al.(1989), who observed only 17.6% inhibition with NBPT at 2 d in a Whitton soil, which had a similar rate of urea hydrolysis as measured in this experiment. The effectiveness of NBPT decreased from 81.5% inhibition at 1 d to 56.7% inhibition at 2 d. Bremner et al. (1991) demonstrated that the inhibitory effect of NBPT was persistent at 30 °C for 28 days, but in this study

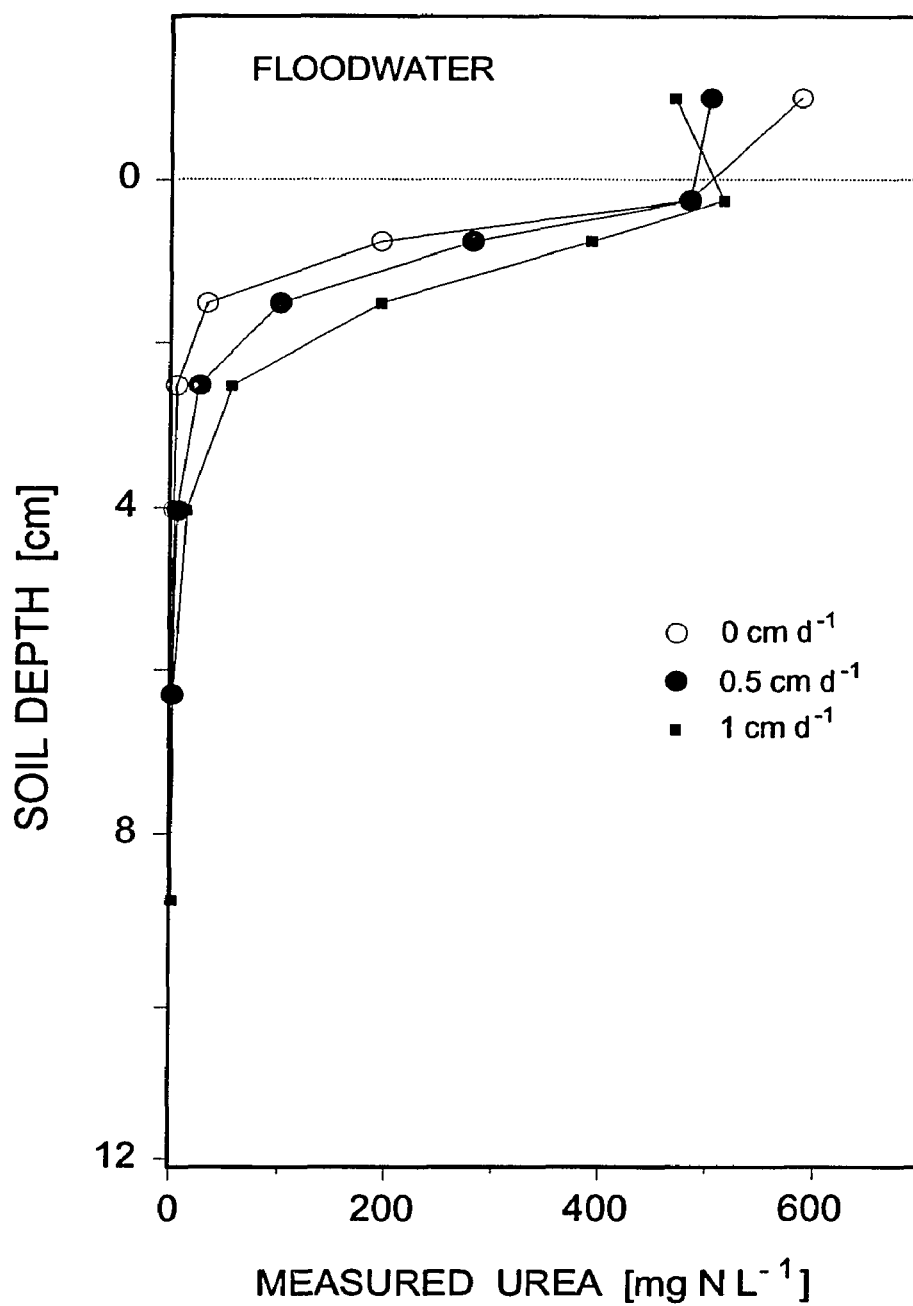


Fig. 13a. Effects of percolation rates and urease inhibitor on urea distribution in flooded Crowley silt loam soil columns incubated for 0.5 d after urea application.

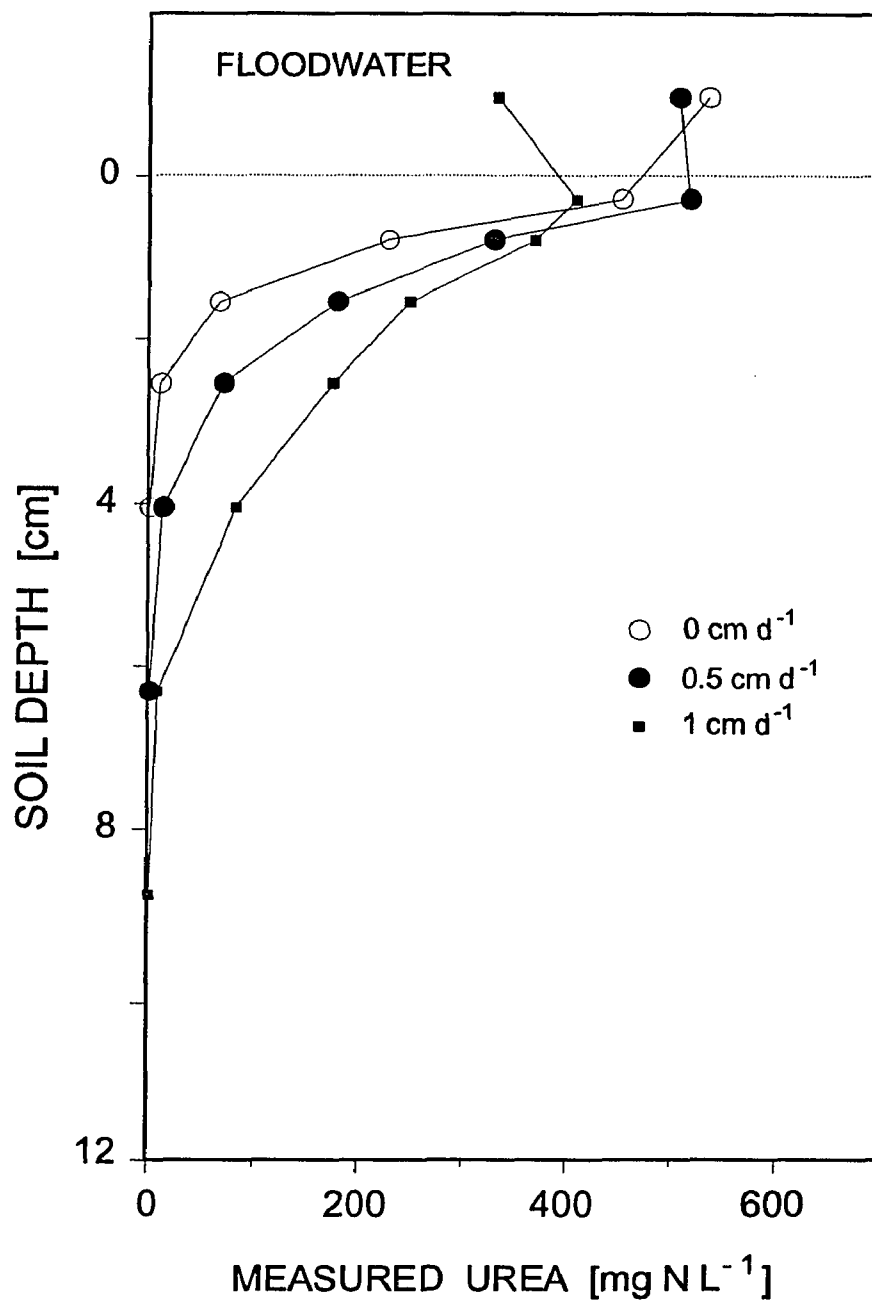


Fig. 13b. Effects of percolation rates and urease inhibitor on urea distribution in flooded Crowley silt loam soil columns incubated for 1 d after urea application.

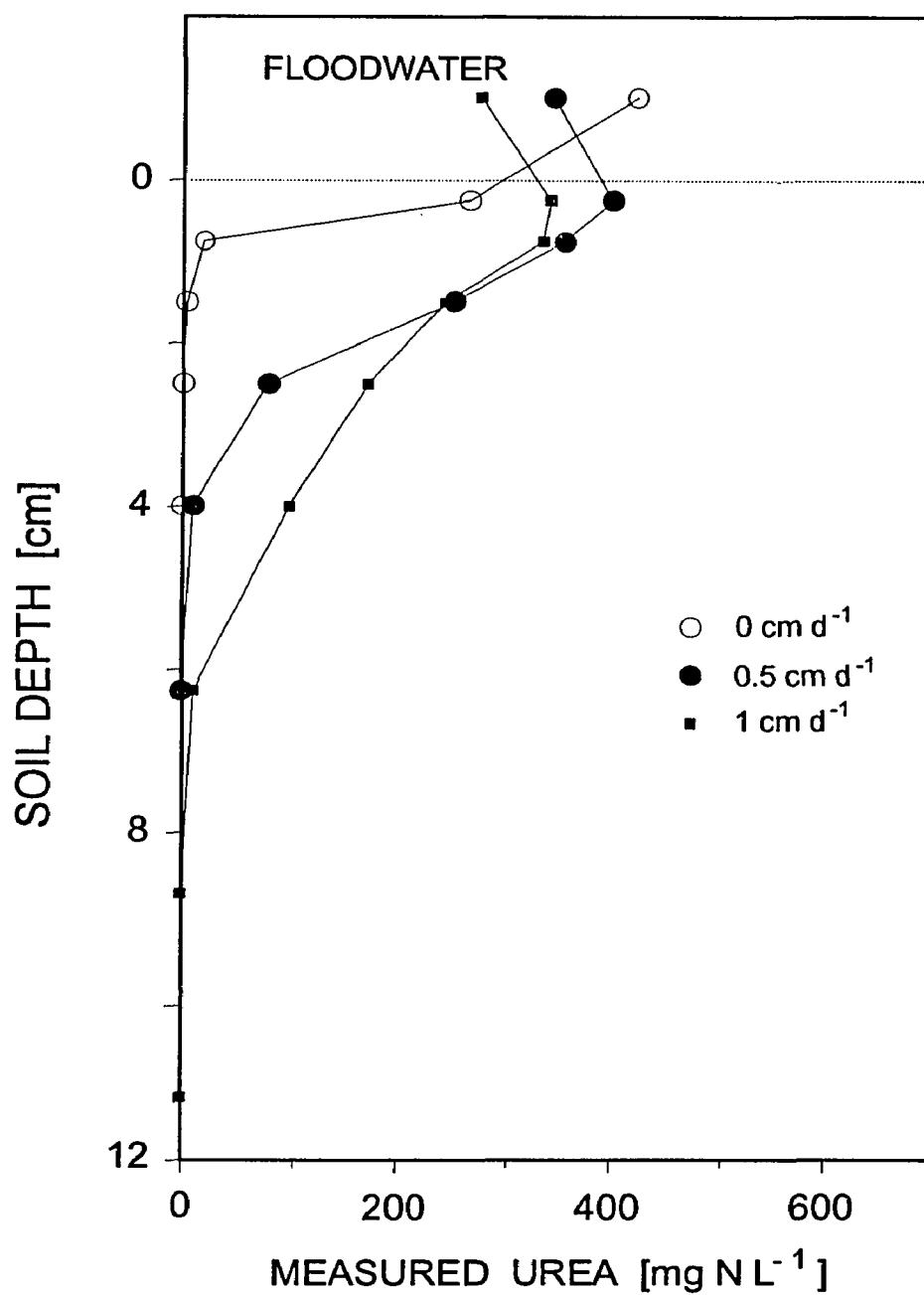


Fig. 13c. Effects of percolation rates and urease inhibitor on urea distribution in flooded Crowley silt loam soil columns incubated for 2 d after urea application.

Table 11. Effects of urease inhibitor (NBPT) and percolation rates on distribution of urea-N, NH_4^+ -N, and NO_3^- -N in flooded Crowley silt loam soil columns during 2 d after urea application.

Incubation periods (days)	Layers (cm)	Percolation rates								
		0 cm d ⁻¹			0.5 cm d ⁻¹			1 cm d ⁻¹		
		UREA-N (mg-N)	NH_4^+ -N (mg-N)	NO_3^- -N (mg-N)	UREA-N (mg-N)	NH_4^+ -N (mg-N)	NO_3^- -N (mg-N)	UREA-N (mg-N)	NH_4^+ -N (mg-N)	NO_3^- -N (mg-N)
0.5	floodwater	55.24	0.49	1.63	51.06	0.38	1.54	45.65	0.36	1.29
	0-0.5	9.39	0.74	0.17	9.15	0.65	0.08	11.02	0.55	0.08
	0.5-1	2.51	0.45	0.06	4.27	0.50	0.35	4.65	0.05	0.01
	1-2	0.71	0.47	0.00	2.51	1.09	0.27	4.77	0.51	0.05
	2-3	0.08	0.00	0.00	0.53	0.40	0.10	1.33	0.15	0.02
	3-5	0.07	0.17	0.04	0.20	0.80	0.89	0.60	0.00	0.00
	5-7.5	0.00	0.01	0.00	0.00	1.21	0.07	0.06	0.39	0.00
	7.5-10	0.00	0.13	0.00	0.00	0.38	0.00	0.00	0.55	0.00
	10-12.5	0.00	0.00	0.00	0.00	0.32	0.00	0.00	0.33	0.00
	TOTAL	68.00	2.46	1.91	67.71	5.72	3.30	68.08	2.90	1.46
1	floodwater	50.85	0.69	1.39	44.95	0.82	0.74	40.95	0.56	0.66
	0-0.5	9.13	1.04	0.14	11.03	1.09	0.02	9.25	0.08	0.00
	0.5-1	3.06	1.54	0.03	4.37	1.66	0.00	5.01	0.18	0.00
	1-2	1.46	1.15	0.05	3.67	1.72	0.00	5.67	0.38	0.00
	2-3	0.22	0.08	0.10	1.53	1.01	0.00	3.89	0.56	0.05
	3-5	0.00	0.00	0.00	0.56	0.19	0.00	3.52	0.00	0.00
	5-7.5	0.00	0.00	0.00	0.00	0.33	0.00	0.45	0.00	0.00
	7.5-10	0.00	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	10-12.5	0.00	0.00	0.00	0.00	0.00	0.46	0.00	0.00	0.00
	TOTAL	64.72	4.67	1.72	66.11	6.83	1.21	68.73	1.76	0.71
2	floodwater	37.62	2.59	1.19	30.69	0.49	0.90	19.69	0.15	0.44
	0-0.5	5.15	11.00	0.16	7.72	3.35	0.05	5.53	0.92	0.02
	0.5-1	0.29	9.22	0.07	5.09	4.30	0.00	4.46	0.88	0.03
	1-2	0.11	6.57	0.00	5.75	9.29	0.09	5.94	4.36	0.00
	2-3	0.03	1.84	0.27	2.01	7.25	0.05	4.05	2.98	0.03
	3-5	0.02	1.66	0.77	0.41	0.05	0.00	4.64	3.57	0.00
	5-7.5	0.00	0.99	0.41	0.00	0.37	0.00	0.61	2.41	0.00
	7.5-10	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00
	10-12.5	0.00	0.92	0.00	0.00	0.00	0.00	0.00	0.00	0.28
	TOTAL	43.23	34.80	2.87	51.66	25.10	1.10	44.95	15.26	0.79

the high activity of urease in the Crowley silt loam soil may have diminished NBPT effectiveness.

Percolation rates exhibited a strong effect on mobility of urea (Figure 13(a-c)). The highest percolation rate had the highest concentration of urea in each soil layer at 0.5 d. As incubation continue, higher concentrations of urea were accumulated in each layer. Total urea accumulation in the soil column at 1 d was found to be 13.87, 21.16, and 27.8 mg urea-N with percolation rates of 0, 0.5, and 1 cm d⁻¹, respectively. For the leading edge of the urea diffusion front at 1 d, urea was found in the 2- to 3-cm, 3- to 5-cm, and 5- to 7.5-cm soil layers for percolation rates of 0, 0.5, and 1 cm d⁻¹, respectively. The diffusion front of urea extended into the 7.5- to 10-cm layer at 2 d with a percolation rate of 1 cm d⁻¹ but without percolation, urea only moved into the 3- to 5-cm layer. The results show that for a water percolation rate of 1 cm d⁻¹ the distance the urea front moved into the soil was doubled and the amount of urea moving into the soil increased from 5.6 to 25.25 mg urea-N compared to the zero flow at 2 d.

The concentration profiles of NH₄⁺-N (Figure 14(a-c)) conformed with the hydrolysis of urea. Very low amounts of NH₄⁺-N were measured at 0.5 and 1 d after urea application. A more pronounced formation of NH₄⁺ occurred after 2 d of incubation where approximately one third of the applied urea had been hydrolyzed. Percolation rate exhibited a greater effect on distribution of NH₄⁺-N in soil columns containing NBPT compared to columns without NBPT (Figure 12(a-c)) because the water carried not only the NH₄⁺-N but also unhydrolyzed urea into the deeper soil layers before hydrolysis occurred. The concomitant movement of urea and NH₄⁺-N

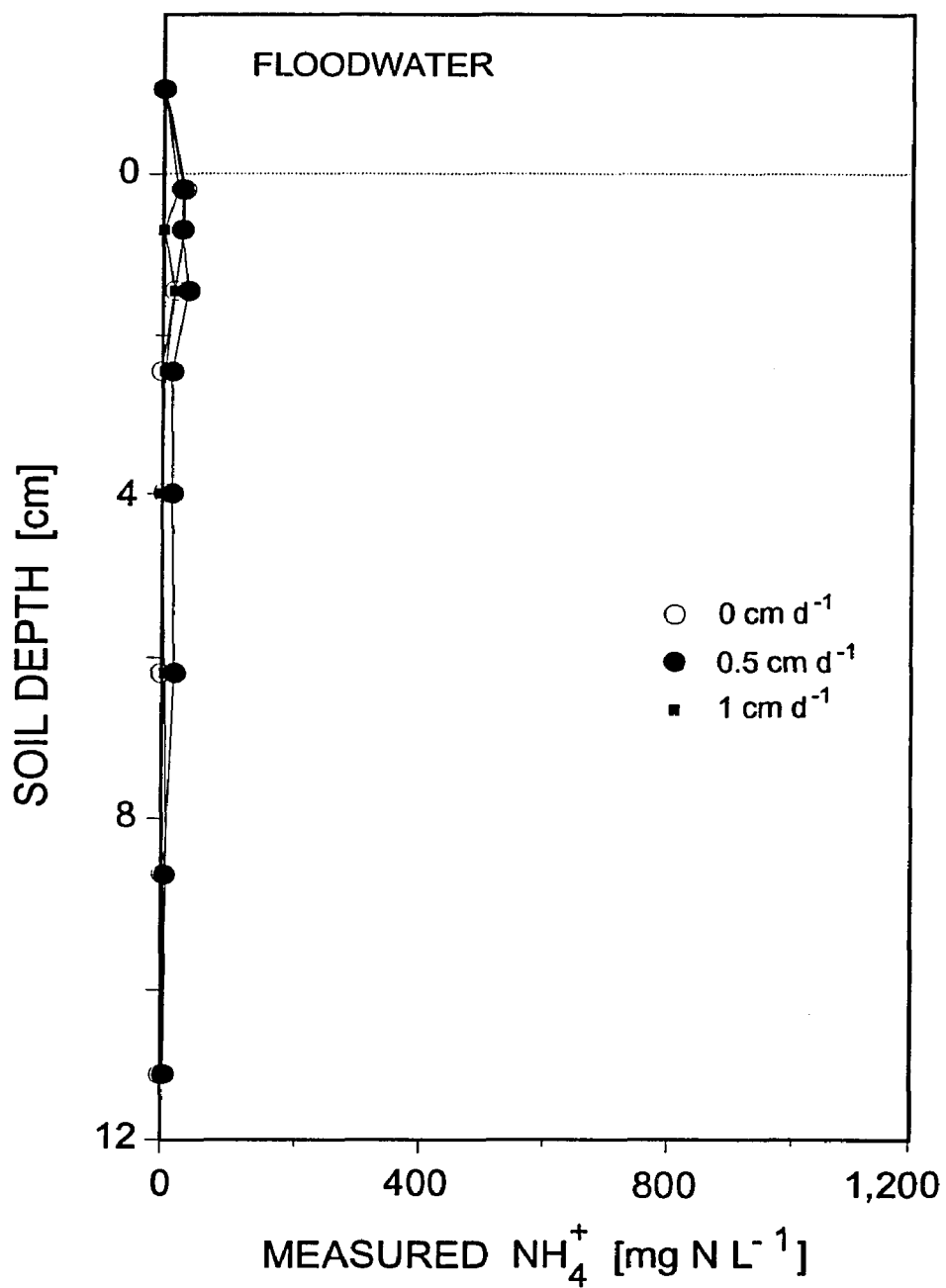


Fig. 14a. Effects of percolation rates and urease inhibitor on NH_4^+ -N distribution in flooded Crowley silt loam soil columns incubated for 0.5 d after urea application.

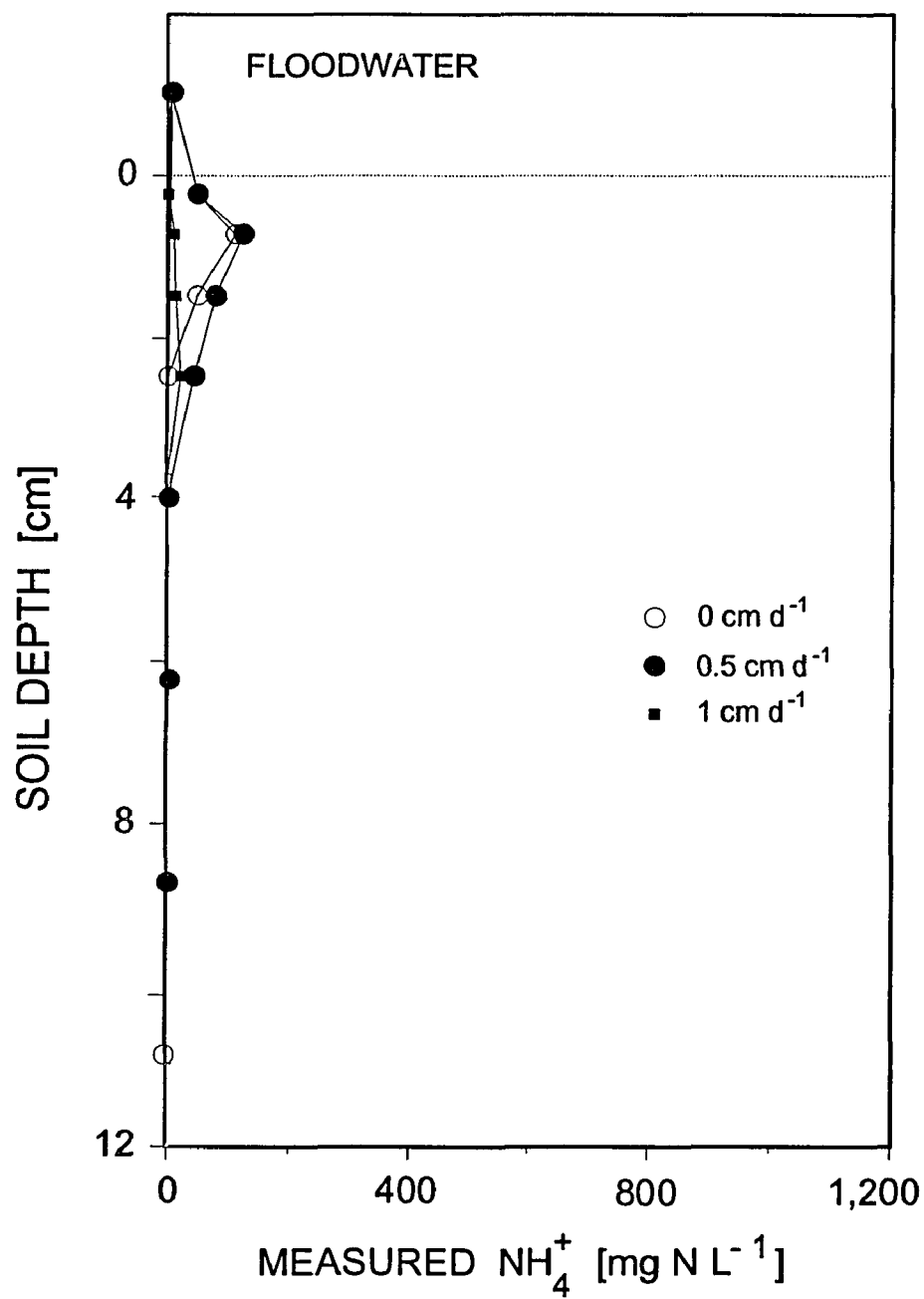


Fig. 14b. Effects of percolation rates and urease inhibitor on NH_4^+ -N distribution in flooded Crowley silt loam soil columns incubated for 1 d after urea application.

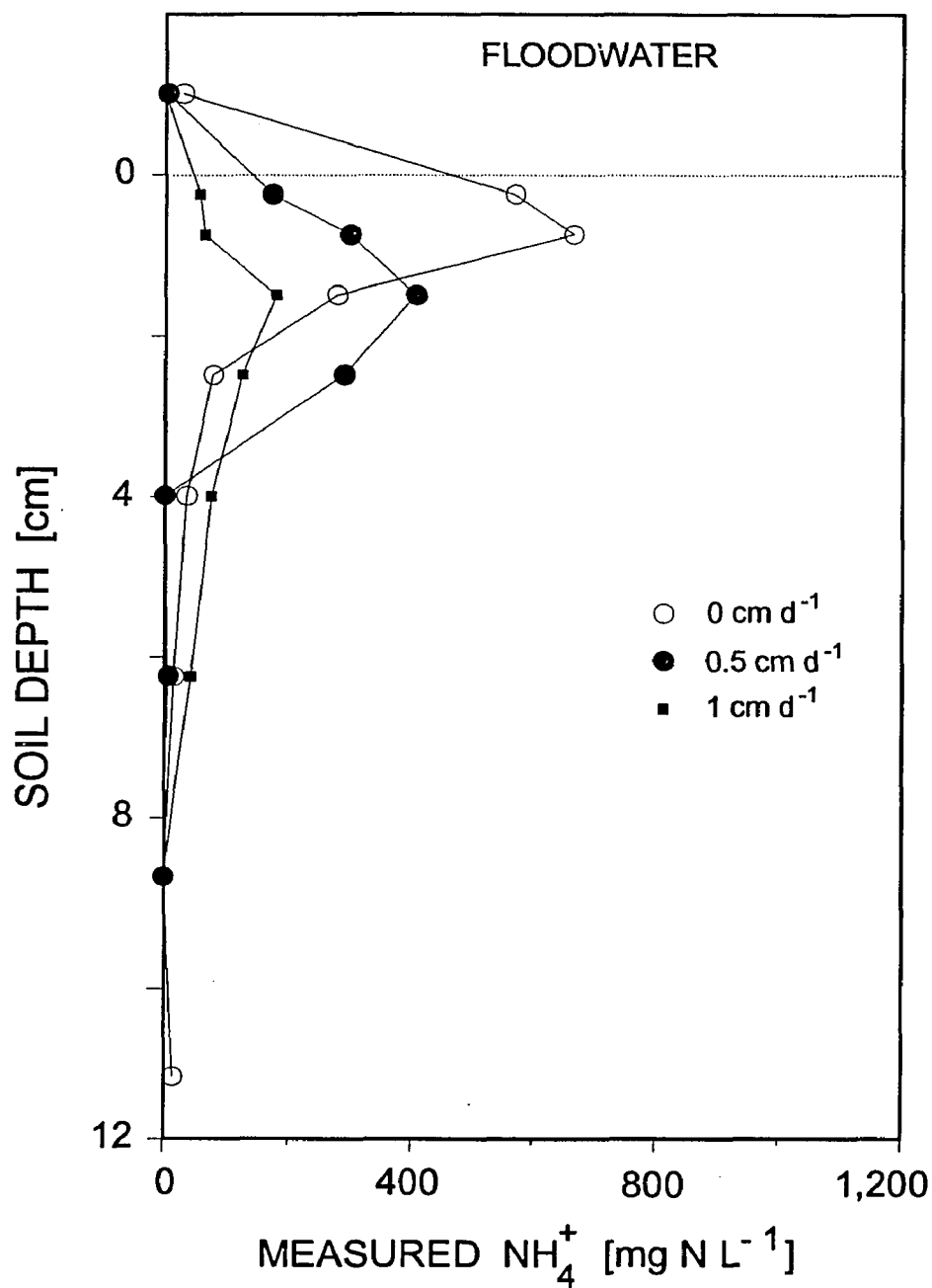


Fig. 14c. Effects of percolation rates and urease inhibitor on NH_4^+ -N distribution in flooded Crowley silt loam soil columns incubated for 2 d after urea application.

resulted in a flatter curve of $\text{NH}_4^+\text{-N}$ distribution than was observed for $\text{NH}_4^+\text{-N}$ in columns without NBPT where the NH_4^+ was mainly translocated from the upper soil layers.

It was found that the movement of N from the floodwater into the soil depended mostly on the urea and $\text{NH}_4^+\text{-N}$ forms. Even though $\text{NO}_3^-\text{-N}$ is easier to leach than the two other forms, its concentration was very low compared to urea and $\text{NH}_4^+\text{-N}$. It appeared that $\text{NO}_3^-\text{-N}$ has only a minor effect on the total distribution of N from applied urea. However, $\text{NO}_3^-\text{-N}$ may play a key role in N loss through denitrification which was not investigated in this experiment. Influence of percolation on distribution of N was more pronounced on urea than $\text{NH}_4^+\text{-N}$ since urea has a lower affinity to be sorbed by the soil (Hongprayoon et al., 1991) than $\text{NH}_4^+\text{-N}$ (Table 7) and the formation of $\text{NH}_4^+\text{-N}$ also depended on the rate of urea hydrolysis.

Percolation rates mainly affected the mass transport rather than the intrusion of the diffusion front into deeper soil layers for both urea and $\text{NH}_4^+\text{-N}$. The effectiveness of NBPT in retarding urea hydrolysis was relatively high and an average of 66.2% of the applied urea remained in the soil columns after 2 d of incubation. High percolation rate together with the application of the urease inhibitor NBPT moved 39.5% of the applied urea-N into the soil within 1 d after urea application. Using the urease inhibitor in soil with high hydraulic conductivity, however, may enhance leaching loss.

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CONCLUSIONS

Inefficiency of recovering applied N fertilizer by rice in flooded soil is caused, in part, by N loss pathways in the soil and rice rhizosphere. Urea which is the main N fertilizer used by rice producers, also encounters an additional N loss because hydrolysis increases the pH of the surrounding environment which can cause high losses through NH_3 volatilization. Many techniques have been tried to reduce urea-N losses including retardation of urea hydrolysis using urease inhibitors. To improve the rice uptake efficiency of urea-N or to develop better cultural practices, however, requires more detailed information about the transformations and distribution of N from applied urea in flooded soil under various conditions. To obtain a better understanding with regard to urea transformations in flooded soil, the experiments in this study were designed to investigate the rates of urea hydrolysis, urea diffusion, urea adsorption, and the subsequent distribution of NH_4^+ -N and NO_3^- -N under aerobic and anaerobic conditions. The effects of the urease inhibitor (NBPT) and percolation rates were also studied to investigate the transformations and movement of N from applied urea.

The adsorption of urea in Crowley silt loam soil was found to have an average adsorption coefficient value of about 5.1×10^{-2} . The adsorption coefficient, which was defined as the ratio between urea adsorbed on soil and the urea concentration in equilibrium solution, depended on the concentration of added urea and increased with increasing concentration of added urea-N. Because urea adsorption was relatively low

in the Crowley silt loam soil, it was considered to have only a minor role and had no significant role in urea movement. The adsorption of urea in other soils, however, may have more of a significant role in urea movement if the adsorption coefficients are higher.

In the investigation of urea diffusion in soil, the hydrolysis of urea had to be completely inhibited to ensure that the changing of urea concentrations in the soil columns were only the result of diffusion. The combination of autoclaving the soil together with the urease inhibitor (NBPT) was found to be an effective treatment which completely inhibited hydrolysis of urea for 6 d. The diffusion coefficient of urea in the soil columns without hydrolysis was estimated by using finite-difference equations to describe the urea movement. The best fit value for the urea diffusion coefficient for measured and calculated data was $3.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. At 6 d after urea application, 39% of the urea applied to the floodwater was found to have diffused into the soil and about 61% remained in floodwater. The urea diffusion front moved to the 7.5- to 10-cm soil depth within 4 d. In nonsterile soil columns where urease activity was not inhibited, urea hydrolyzed rapidly and disappeared within 4 d after urea addition. The rate of hydrolysis increased with incubation time and was higher in the soil than in the floodwater. With this high rate of hydrolysis, urea was never detected in layers lower than 2 cm from the soil surface during the six days of the experiment. It was assumed that the soil and/or soil-floodwater interface are the main sites for urea hydrolysis. This experiment demonstrated that if urea was not hydrolyzed, about 39% of the applied

urea diffused into the soil within 6 d. Without the use of a urease inhibitor, urea was hydrolyzed rapidly and not detected in the soil columns at 4 d.

The adsorption and fixation of $\text{NH}_4^+\text{-N}$ was studied in Crowley silt loam soil columns. It was observed that the amount of both adsorbed $\text{NH}_4^+\text{-N}$ and fixed $\text{NH}_4^+\text{-N}$ increased with increasing concentration of added $\text{NH}_4^+\text{-N}$ but the percentage of adsorption and fixation decreased as the concentration of added $\text{NH}_4^+\text{-N}$ increased. The average of adsorbed $\text{NH}_4^+\text{-N}$ and fixed $\text{NH}_4^+\text{-N}$ ranged from 45.9 to 61.6% and 16.7 to 23%, respectively, when the concentration of added $\text{NH}_4^+\text{-N}$ ranged from 100 to 1200 mg N L⁻¹.

The distributions of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ under aerobic and anaerobic conditions did not show different patterns. Measured $\text{NO}_3^-\text{-N}$ concentrations in the aerobic soil columns were very low. The rate of $\text{NH}_4^+\text{-N}$ diffusion was estimated using finite-difference equations and was found to be $3.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. This was the same as the estimated rate of urea diffusion, and it seemed reasonable since diffusion of solutes was expressed in terms of solution phase where the total solute per layer included both the adsorbed form and solute in soil solution.

Percolation rates and the urease inhibitor NBPT exhibited strong effects on distribution of urea and $\text{NH}_4^+\text{-N}$ in flooded soil columns. The effect of percolation without NBPT addition was more pronounced on urea movement at 0.5 d after urea application because urea was hydrolyzed rapidly after 1 and 2 d. Formation of $\text{NH}_4^+\text{-N}$ in the columns without NBPT also confirmed the high rate of hydrolysis of urea and as urea hydrolyzed increased, $\text{NH}_4^+\text{-N}$ increased in the soil profile. The use of NBPT

slowed urea hydrolysis dramatically for all percolation rates and also enhanced the effect of percolation. Distribution patterns of both urea and $\text{NH}_4^+\text{-N}$ in the columns with NBPT differed considerably compared to columns without NBPT. Less hydrolysis occurred and urea moved into deeper soil layers when NBPT was present. Percolation affected mainly mass transport of urea and $\text{NH}_4^+\text{-N}$ rather than the intrusion of the diffusion fronts into deeper soil layers. The effectiveness of NBPT in retarding urease activity was high for the first day and the average percentage inhibition was 81.5% but diminished to 56.7% after 2 d.

VITA

Chawalit Hongprayoon was born on August 9, 1952 in Chiang Rai, Thailand. He received a B.S. in Soil Science with honors from Kasetsart University in 1974. In 1980, he obtained a Master of Science degree with a major in Microbiology from Kasetsart University. After graduation, he worked as an instructor in the Department of Soil Science, Kasetsart University. He is presently a candidate for the Doctor of Philosophy degree in Agronomy with a minor in Microbiology.

DOCTORAL EXAMINATION AND DISSERTATION REPORT


Candidate: Chawalit Hongprayoon

Major Field: Agronomy


Title of Dissertation: Urea Transformations in Flooded Soil


Approved:

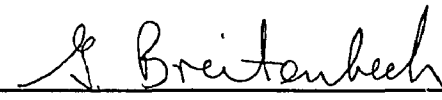

Major Professor and Chairman

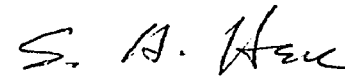

Dean of the Graduate School

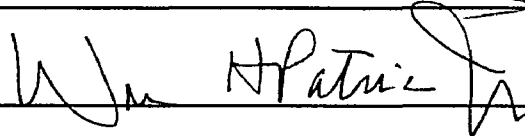
EXAMINING COMMITTEE:











Date of Examination:

10/29/92