UREA HYDROLYSIS IN SEMI-ARID TROPICAL ALFISOLS AND VERTISOLS

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CERTIFICATE

Mr.G.W.L. Jayakumar has satisfactorily prosecuted the course of research and that the thesis entitled UREA HYDROLYSIS IN SEMI-ARID TROPICAL ALFISOLS AND VERTISOLS submitted is the result of original research work and is of sufficiently high standard to warrant its presentation to the examination. I also certify that the thesis or part thereof has not been previously submitted by him for a degree of any University.

Date: 18 December 1991

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This is to certify that the thesis entitled UREA HYDROLYSIS IN SEMI-ARID TROPICAL ALFISOLS AND VERTISOLS, submitted in partial fulfilment of the requirements for the degree of "Doctor of Philosophy" in Agriculture of the Andhra Pradesh Agricultural University, Hyderabad, is a record of the bonafide research work carried out by MR. G.W.L. JAYAKUMAR under my guidance and supervision. The subject of the thesis has been approved by the Student's Advisory Committee.

No part of the thesis has been submitted for any other degree or diploma. The published part has been fully acknowledged. All assistance and help received during the course of the investigations have been duly acknowledged by the author of the thesis.

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DECLARATION

I declare, that this thesis entitled UREA HYDROLYSIS IN SEMI-ARID TROPICAL ALFISOL AND VERTISOL is a bonafide record of work done by me during the period of research at ICRISAT, Patancheru. This thesis has not formed in whole or in part, the basis for the award of any degree or diploma.

Date: 18 December 91

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ABSTRACT

Urea hydrolysis rates in the field have been rarely measured and not at all in India, in contrast to the numerous measurements in laboratory experiments. This study was therefore commenced to investigate the feasibility of measuring hydrolysis rates in the field, then to compare these with laboratory measurements with the aim of assessing the prediction of urea hydrolysis rates in the field from laboratory determinations.

In a series of four experiments in the field on the benchmark Alfisol and Vertisol at ICRISAT Center, urea hydrolysis was measured after application of urea to the soil by analysing the soil samples to determine the disappearance

of urea. Initially, crystalline urea was spread uniformly on the soil surface in plots of 4 m^2 area before (Experiment 1) or after (Experiment 2) irrigating the soil, and this area was sampled at intervals using a core sampler. Subsequently (Experiments 3 and 4) urea in solution was uniformly mixed with the surface 0-5 cm depth of soil inside small (7-cm diam.) confined microplots and hydrolysis was measured by destructive sampling at regular intervals. In the incubation experiment, urea was incubated with soil at constant environmental conditions of temperature (32°C) and moisture content (24 per cent, Alfisol; 40 per cent, Vertisol).

The field and the incubation experiments showed that urea hydrolysis was rapid in these two soils, especially in the microplot experiments in which over 90 per cent of the applied urea-N was hydrolysed within 24 hours of its application. Urea hydrolysis generally followed a first order reaction more closely than a zero order reaction in all experiments. Urea hydrolysis rates were similar in the microplot experiments (12-16 per cent urea-N h^{-1}) and the laboratory experiment (11-17 per cent urea-N h^{-1}), but were greater than in the first two field experiments (0.9-3.6 per cent urea-N h^{-1}). The slower rate in the latter is attributed to the time required for dissolution of surface applied urea and lack of contact with urease enzyme.

The microplot method of experimentation was found to be more suitable for measuring urea hydrolysis rates in the field than the sampling of larger (4 m^2) plots. The

accumulation of NH_4^+-N, NO_2^--N and NO_3^--N in soils and the disappearance of urea could be measured with better precision, and the recoveries of nitrogen were better.

The comparison between the data from the microplot experiments and laboratory incubation studies indicated that urea hydrolysis rates in the field could be predicted from the laboratory studies. This finding has to be examined further with detailed experimentation. Further experiments are also required to relate urease activity with soil variables such as organic carbon and clay content, so that more general relationships can be generated in the present study to prepare models for predicting urea hydrolysis in agricultural soils.

LIST OF SYMBOLS AND ABBREVIATIONS

mm	millimeter
cm	centimeter
m	meter
ug	microgram
mg	milligram
kg	kilogram
ml	milliliter
L	Liter
cm^2	square centimeter
m^2	square meter
ha	hectare
h	hour
kg ha^{-1}	kilogram per hectare
^oC	centigrade
ppm	parts per million
mg kg^{-1}	milligram per kilogram
M	molar
C mole kg^{-1}	centimole per kilogram

INTRODUCTION

CHAPTER I

INTRODUCTION

Urea is the most widely used solid nitrogen fertilizer in the world agriculture. The outstanding feature of this fertilizer that has led to its popularity is its high content of nitrogen (46 per cent N), favorable economics of manufacturing, handling, storage and transportation.

Urea applied to soil is hydrolysed to ammonia and carbon dioxide by urea enzyme. Ammonium thus produced may be oxidised to nitrite and nitrate. Hydrolysis an enzymatic reaction is very critical for the use of urea as a fertilizer, because it converts urea nitrogen into a form which can be utilized readily by plants. Thus studies on urea hydrolysis are important for predicting the availability of nitrogen to crops.

The factors influencing urea hydrolysis in soils have been extensively studied. The review of literature indicates that, among the many factors that affect urea hydrolysis in soil, the most important are soil moisture (Delaune and Patrick, 1970; Gould et al., 1973; Sahrawat, 1984), temperature (Gould et al., 1973; Dalal, 1975a; Pettit et al., 1976; Sahrawat, 1984), organic carbon (Dalal 1975a; Zantua et al., 1977; Beri and Brar, 1978), soil pH (May and Douglas, 1976; Pettit et al., 1976), and clay content and cation exchange capacity (Hagin and Tucker, 1982). However, almost

all the information on urea hydrolysis has come from the laboratory studies.

In contrast to the large information from laboratory studies relatively few investigators have studied the rate of urea hydrolysis in the field (Gould et al., 1986), especially under semi-arid tropical environments. The general lack of comparison of rates in the field with those in the laboratory and lack of testing of the basic concepts in the field, applies particularly to India where urea hydrolysis rates in the field have not been reported. Gould et al. (1986) stated that laboratory studies have improved our understanding of the urease activity in soils, but they do not simulate field conditions; and, in order to improve the use efficiency of urea as a fertilizer, it is necessary to understand the transformations of urea under field conditions. Lack of precise techniques for studying urea hydrolysis in the field has been a hindrance to conducting such research. The usual soil sampling methods in the field measurements, are laborious and can be associated with appreciable sampling errors. Also, there is a need to compare urea hydrolysis rates in the field with those obtained from laboratory assay on soil from the same site.

The present study was therefore initiated to develop techniques for measuring urea hydrolysis rates in the field, and to compare the field rates with those obtained in the laboratory under similar conditions of temperature and soil moisture. Such calibrations could allow the application of

basic concepts built up from laboratory studies for prediction of urea hydrolysis rates in the field.

REVIEW OF LITERATURE

CHAPTER II

REVIEW OF LITERATURE

2.1 UREA HYDROLYSIS

Urea added to soil is hydrolysed by the urease enzyme.

$$CO(NH_2)_2 + 2H_2O \xrightarrow{\text{urease}} (NH_4)_2\,CO_3$$

$$(NH_4)_2\,CO_3 \xrightarrow{\text{decomposes}} 2NH_3 + CO_2 + H_2O$$

In the presence of adequate water or other H^+ donors, ammonia is converted to ammonium ion.

2.2 UREASES

Urease is the commonly used group name for enzymes which catalyze hydrolysis of urea, by acting on C-N bonds (non-peptide), in linear amides. These enzymes are classified as urea amide hydrolases, E.C.3:5.1.5 (Riethel, 1971; Ladd and Jackson, 1982).

Urease was first crystallized by Sumner in 1926 from jackbean (*Canavalia ensiformis* (L.) DC) (Gould et al., 1986). The urease molecule contains sulphydyl (-SH) groups essential for its activity and substrate specificity is high. It also has two essential atoms of bound Ni^{2+} per enzyme molecule (Ladd and Jackson, 1982).

Most of the knowledge concerning the urease enzyme has come from experiments conducted with urease enzyme in jackbean

(Bremner and Mulvaney, 1978). In their review, Bremner and Mulvaney (1978) tabulated data on the Michaelis constant (Km), activation energy (Ea), and optimum pH for urease extracted from soybean, jack bean, bacteria and soil. They concluded that ureases from different sources differ in their properties, especially soil urease. It appears to be much more difficult to get reliable kinetic data for enzymes present in a heterogenous medium such as soil than for enzymes in homogenous solutions.

This review covers soil urease, the kinetics of urea hydrolysis in soils, and the assay techniques for studies on urea hydrolysis in both laboratory and field experiments.

2.3 SOIL UREASE

The fate and effectiveness of fertilizer urea is very much determined by the urease activity in soils (Kiss et al., 1975; Bremner and Mulvaney, 1978). Urease activity in soil is due to extracellular enzymes as well as those enzymes within the proliferating microorganisms (Kiss et al., 1975). These authors described the extracellular enzymes that accumulate in soil as "free enzymes" or "exoenzymes". They are derived from ruptured moribund cells. (McGarity and Myers, 1967). This enzyme, which catalyzes urea hydrolysis occurs universally and is abundant in soils (Tisdale et al., 1985).

Rotini (1935) discovered the presence of urease in soils (Bremner and Mulvaney, 1978). Conrad (1940a,b, 1942a,b) provided confirmatory evidence, and indicated its importance in conversion of urea to ammonia. Briggs and Segal (1963) isolated urease in crystalline form from soil; they found that it was a mixture of proteins exhibiting urease activity. Burns et al. (1972a,b) isolated a clay free organic fraction from soil which exhibited urease activity.

The urease in soils appears to be primarily of microbial origin. Sumner (1953) reported that urease is found in most species of bacteria, yeast, fungi, and plants. Soil microorganisms such as bacteria, actinomycetes, and fungi are capable of synthesizing urease (Seneca et al., 1962; Roberge and Knowles, 1967). A small group of bacteria known as ureolytic bacteria have high ability to synthesize urease (Tisdale et al., 1985). The bacteria which can synthesize urease include aerobes, microaerophiles and anaerobes (Roberge and Knowles, 1967; Lloyd and Sheaffe, 1973). Kiss et al. (1975) stated that the sources of accumulated extracellular urease are primarily microbial cells, and that enzymes present in soils can also originate from plant and animal residues.

Mahaptra et al. (1977) demonstrated that rice roots release urease into soils. Frankenberger and Tabatabai (1982) reported urease activity in 21 diverse plants from Graminae and Leguminaceae families, which included sorghum (*Sorghum bicolor* (L.) Moench), corn (*Zea mays* L.), and soybean (*Glycine max* (L.) Merr.).

The urease enzyme cannot have a completely independent existence; because, if it is truly free in soils, it should be rapidly inactivated (Bremner and Mulvaney, 1978). Urease in soils is associated with soil constituents, for example by being adsorbed on clay or organic colloids (Conrad, 1940b; Pinck and Allison, 1961; McGarity and Myers, 1967; Paulson and Kurtz, 1969a; Skujins and McLaren, 1969; Dalal 1975a). Kiss et al. (1975) reported that soil urease occurs in the form of a complex with humic substances, and that it is associated primarily with humic substances and secondarily with clays. Pinck and Allison (1961) showed that montmorillonitic clay adsorbed urease with greater efficiency than kaolinitic clay.

Adsorption of urease by soil colloids gives it stability and protection (Conrad, 1940a,b; Skujins and McLaren, 1969; Burns et al., 1972b; Nannipiere et al., 1974; McLaren et al., 1975; Zantua and Bremner, 1976; 1977; Ceccanti et al., 1978). Burns et al., (1972a,b) proposed that protection of urease could be due to immobilization of urease within the organic matter during humus formation. Skujins and McLaren (1969) detected measurable urease activity in Alaskan permafrost soil samples that were over 8700 years old. Zantua and Bremner (1977) did not find any decrease in urease activity when field moist soils were air dried and stored at 21-23^{o}C for two years. The amendment of soils with organic materials increased urease activity, but only temporarily; subsequently, the activity declined to become similar to that of the

unamended soils (Zantua and Bremner 1976). They concluded that every soil has a stable level of urease activity determined by the ability of its constituents to protect this enzyme. Because of the adsorption of urease by soil colloids and subsequent stability, extracellular urease is responsible for most of the urea hydrolytic activity in soil. Paulson and Kurtz (1969a) attributed 79 to 89 per cent of the urease activity in a silty clay loam soil to the adsorbed extracellular urease. Pettit et al. (1976) considered that 60 per cent of the total urease activity was due to the extracellular bound enzyme and the remainder was due to extracellular unbound and intracellular ureases.

2.4 KINETICS OF UREA HYDROLYSIS

The kinetic properties of the urease enzyme include Michaelis-Menten constants, activation energy values, (Ea) and the orders of the hydrolysis reaction. These properties vary widely for different soils because of different potential sources of enzymes and likelihood of heterogeneous distribution of enzymes in the soils. The kinetic properties of the urease enzyme have been studied almost entirely in the laboratory.

2.4.1 Michaelis-Menten Constants

The Michaelis-Menten constant (Km) represents the combined rate constants of three reactions involved in enzyme catalysed chemical reactions i.e., formation of enzyme-substrate complex (k+1), dissociation of enzyme substrate complex (k-1), and formation of product (k+2)

$$Km = \frac{k+2 \times k-1}{k+1}$$

The velocity or rate of reaction can be represented by

$$\frac{(k+2)e}{(Km/s)+1}$$

wherein e = total concentration of enzyme both in free and complex forms and S = concentration of free substrate.

When the concentration of substrate is high, all the enzyme present will form a complex with the substrate, and under such conditions the velocity of a reaction will attain a maximum rate of velocity 'Vmax'.

$$\text{Then} \quad v = \frac{Vmax}{(Km/s)+1} = \frac{Vmax\ S}{Km + s}$$

This is the equation used for calculating Km in an enzymatic reaction.

The experimental value of Michaelis-Menten constant for any enzyme corresponds to that concentration of the substrate at which the rate of reaction becomes half of the maximum velocity rate Vmax.

$$\text{At that time} \quad v = \frac{Vmax}{2} \times \frac{Vmax(s)}{Km + S}$$

or $Km + S = 2S$
or $Km = S$

$$S/V = Km/Vmax + (1/Vmax)(S)$$
$$= Km/Vmax + S/Vmax$$
$$= 1/Vmax\ (Km+S)$$

The Km and Vmax values were computed by plotting S/v against substrate concentration (S) the slope was 1/Vmax and the intercept was Km/Vmax Beri et al. (1978) observed that the Michaelis-Menten equation is normally applicable only to well defined homogeneous systems involving enzymatic reactions; and that there are serious limitations to the determination of Km and Vmax values in heterogeneous systems like soils, because the Km and Vmax values calculated from Michaelis Menten equation by Paulson and Kurtz (1970) and Tabatabai (1973) have not shown the expected inverse relationship between the two values. Beri et al. (1978) calculated Km and Vmax values for urease in soils by using two equations, i.e., the Michaelis-Menten equation and the integrated form of Michaelis-Menten equation. The integrated form of Michaelis-Menten equation used was

$$(So-S)/t = Vmax + Km\ (\ln S/So)\ 1/t$$

So = substrate concentration at zero hour (to)

S = the amount of urea hydrolysed at a given time (t)

A plot of (So-S)/t against 1/t ln S/So gave an intercept of Vmax and the slope was Km. According to them Beri et al. (1978) using the equation developed by integration of Michaelis-Menten equation over reaction period (to-t) to calculate Km and Vmax values gave these values which bore a close relationship (r=-0.88).

The Km values for soil urease activity reported vary from 2.75 x 10^{-6} M (Pal and Chhonkar, 1979) to 210 x 10^{-3} M (Paulson and Kurtz, 1970) in soils from different agroclimatic regions. Patra and Jain (1984) determined that 8.33 μ moles of urea N g^{-1} h^{-1} was the critical concentration to attain the maximum velocity rate of 0.49 μ moles urea hydrolysed g^{-1} h^{-1}, for a Typic Ustochrept.

In surface soils from Iowa, Tabatabai (1973) did not find any significant correlation between Km values and pH, organic carbon, clay, silt, or sand fraction. He also reported that Km values of the soil urease were similar to those of urease in different particle size fractions of the soil. Pal and Chhonkar (1979) reported a significant positive correlation of Km values with soluble salt content, and concluded that it was due to the deleterious effect of soluble salts on the enzyme. Pettit et al. (1976) stated that Km values for soil extracts exceeded those of soils.

While Paulson and Krutz (1970), Tabatabai (1973), and Rachhpal-Singh and Nye (1984a and b) determined Km values for soil urease in temperate regions, Beri and Brar (1978) and Pal and Chhonkar (1979) determined Km values for soil urease in semi-arid regions of Punjab (India). Based on the Km values, Beri and Brar (1978) concluded that ureases produced in soils of temperate and semi-arid regions are similar.

The variation in Km and Vmax values in urease activities of different soils is attributed to ureases of different

origin, the diffusion of urea to the sites of bound ureases (Ladd and Jackson, 1982), fluctuations in microbial population and concurrent changes in microbial and adsorbed urease (Paulson and Kurtz, 1970), soil properties such as organic carbon, pH, and clay content (Beri and Brar, 1978; Rachhpal-Singh and Nye, 1984a), and conditions of an assay including methods used for calculations of Km values (Tabatabai, 1973).

2.4.2 Activation Energy Values (Ea)

There are only a few reports about the activation energies (Ea) required for the formation of substrate and enzyme complex, and the subsequent hydrolysis. The mean activation energies of soil ureases range from 3.90 to 24.5 K cal $mole^{-1}$ for different soils (Bremner and Mulvaney, 1978). Dalal (1975b) reported higher activation energy values for the urease in soils in the presence of toluene, and concluded that adsorbed urease has decreased affinity for urea as compared to the microbial urease.

2.4.3 Urea Hydrolysis Reaction Orders

In the field of chemistry, the relationship between the rate of chemical reaction and the concentration of reacting molecules is often expressed as the order of reaction. Chin and Kroontje (1963), Overrein and Moe (1967), Sankhayan and Shukla (1976), Kumar and Wagnet (1984), and Yadav *et al.* (1987) reported that urea hydrolysis followed first order reaction kinetics, which implies that the rate of urea hydrolysis is dependent on urea concentration. Sahrawat

(1980a) concluded that urea hydrolysis followed zero order kinetics upto 12 hours. A zero order reaction is one in which urea hydrolysis is independent of the concentration of reactant molecules. Patra and Jain (1984) observed that urea hydrolysis took place according to zero order reaction during the first few hours, and changed to first order reaction between 4 and 12 hours. Vlek and Carter (1983) showed that urea hydrolysis followed a zero order reaction when urea was uniformly distributed in the soil, but followed a first order reaction on application of prilled urea, which created a heterogeneous system. The first order kinetics was followed by a rapid increase in hydrolysis rate possibly due to a shift to zero order kinetics. Vlek and Carter (1983) concluded that the order of reaction for urea hydrolysis depends on the method of urea application, and that zero and first order equations could be useful in preparing computer simulation models on urea hydrolysis.

Though number of workers have studied kinetic properties of soil urease, Bremner and Mulvaney (1978) stated that it is more difficult to obtain reliable kinetic data for enzymes in heterogeneous environments such as soil than for enzymes in homogeneous solutions. However, there is no information about the kinetics of urea hydrolysis under field conditions.

2.5 FACTORS INFLUENCING UREA HYDROLYSIS IN SOILS

Urea hydrolysis rates vary greatly among soils all over the world. A few examples can be quoted. McGarity and Myers

(1967) reported a wide range in urease activity in soil samples drawn from 5 great soil groups in Australia. Siddaramappa and Rao (1971) reported that among the red, black, and laterite soils of Karnataka state in India the highest urease activity was in laterite soils followed by the red and black soils. Dash et al. (1981) reported highest urea hydrolysis rates in soils from hilly regions, followed by pasture and forest soils. Reynolds et al. (1985) reported that urea hydrolysis was greater in pastures than in cultivated soils. The differences in urease activity of different soil types are due to soil properties such as organic carbon content, pH, clay content and climatic factors such as moisture and temperature.

2.5.1 Moisture Content

Urea hydrolysis takes place in soils at moisture contents ranging from near air dry to waterlogged (Fertiliser Association of India, 1977). Yet the relationships between moisture content and urea hydrolysis are not very clear. Several workers suggested that urease activity is not affected appreciably by soil moisture content (Delaune and Patrick, 1970; Gould et al., 1973; Bremner and Mulvaney, 1978; Wickremasinghe et al., 1981). Delaune and Patrick (1970) found that urea hydrolysis rates were similar in soil at 1/3 atmosphere moisture suction and in waterlogged conditions. Gould et al. (1973) did not find any difference in urea hydrolysis rates in soils at moisture tensions of 1, 0.1 and

less than 0.001 atmosphere. Bremner and Mulvaney (1978) did not record any significant variation in urea hydrolysis rates of soil samples incubated between 1 and 0.001 atmosphere moisture tension. Urea was ammonified more slowly in soil that was dry (near wilting point) than moist at near field capacity (Low and Piper 1961). In a field experiment to study urea efficiency, Volk (1966) applied urea at the rate of 116 lb/ac to the soil surface: if the soil was air dry, 80 per cent of the urea applied did not hydrolyse even after 14 days, but when soil was continuously moist (from a high water table) the urea was hydrolysed completely in 7 days. Malhi and Nyborg (1979) found that the rate of urea hydrolysis increased as moisture tension decreased from 15 to 1/3 bar and the largest change occurring between 15 to 7 bar tension. In Alfisol and Vertisol soils of the semi-arid tropics Sahrawat (1984) did not detect any urease activity in soil samples in which the moisture content was less than -15 bar pressure. Urease activity increased with increase in moisture content from air dry upto field capacity, after which it remained constant. Kumar and Wagnet (1984) reported that increase in moisture content from 25 per cent of field capacity to full field capacity increased urease activity by 15, 29 and 46 per cent in the three different soils.

Some reports indicated that increasing soil moisture content decreased urease activity. Simpson and Melsted (1963) reported a lower urea hydrolysis rate at less than 1 atmosphere than at 1 atmosphere moisture tension. Roberge and Knowles (1968) observed a decrease in urease activity with increasing moisture content from 60 to 140 per cent of maximum water holding capacity. There was an initial increase in urea hydrolysis rate upto 50 per cent water holding capacity and then a decrease in urea hydrolysis rate above 125 per cent of water holding capacity (Dalal, 1975a). Savant et al. (1987b) reported that hydrolysis of urea increased rapidly with an increase in water content to near field capacity, then hydrolysis tended to remain constant with further increases until the soil was flooded when it decreased. The rate of urea hydrolysis increased with increased moisture content from 20 per cent to 100 per cent field capacity and decreased at flooding (Yadav et al. 1987).

2.5.2 Temperature

Urea hydrolysis was observed to take place at temperatures as low as 1-7^{o}C (Baldwin and Ketchson, 1958; Broadbent et al., 1958), but several reports showed that temperatures between 20 and 40^{o}C increased urease activity. Broadbent et al. (1958) reported a slow rate of urea hydrolysis at 7.2^{o}C and a rapid urea hydrolysis rate at 24^{o}C. Fisher and Parks (1958) using temperature controlled chambers reported an increased rate of urea hydrolysis with increase in temperature. Urea hydrolysis rates were 2-6 times greater

at 25°C than at 1°C depending on the soil type (Simpson and Melsted 1963). The rate of urea hydrolysis was 5.4 times higher at 28°C than at 4°C (Overrein and Moe 1967). Gould et al. (1973) observed a linear relationship between urease activity and temperature between 2 and 45°C. Dalal (1975a) calculated the ratios of urease activity at 37°C to those at 27°C and found that they were 3.28 ± 0.33 and 1.32 ± 0.04 for urease activity in the presence and in the absence of toluene, respectively. These studies of Dalal (1975a) illustrated the considerable dependence of urea hydrolysis on temperature. Bremner and Mulvaney (1978) reported that urease activity increased with rise in temperature from 10 to 75°C, but the increase in urease activity was great between 40 and 70°C, and than there was a decline in the urease activity with further rise in temperature from 70 to 80°C. Sahrawat (1984) reported that urease activity increased with increase in temperature from 10 to 60°C in a Vertisol and 70°C in an Alfisol. In these two soils, the urease activity decreased with further increase in temperature and was close to zero at 100°C. Based on reports from Bremner and Mulvaney (1978) and Sahrawat (1984), Gould et al. (1986) concluded that hydrolysis of urea in soils increases with increasing temperature according to Arrhenius equation upto 60 to 70°C, and then decreases rapidly above the temperature range. Yadav et al. (1987) reported the rate constant (K_1) for first order reaction increased with temperature from 10 to 35°C. Marshall et al. (1990) using the Arrhenius equation

estimated the rate of urea hydrolysis at $0^{o}C$, and suggested that 200 kg urea N ha^{-1} when applied to snow would be hydrolysed within 6 days.

2.5.3 Organic Carbon Content

Urease activity in soils increase with the increase in organic carbon content. (Conrad, 1940a; 1942a; Ananthanarayana and Mithyantha, 1970; Gould et al., 1973; Tabatabai, 1973; Dalal, 1975a; Tabatabai, 1977; Zantua et al., 1977; Beri et al., 1978; Bajpai et al., 1984; Kumar and Wagnet, 1984). According to Conrad (1940a; 1942a), soils which received more organic matter through different cropping patterns and cultural practices, and the surface layer of soils exhibited higher urease activitity. Low organic matter content could be one of the factors for low urea hydrolysis rates at a given temperature in light-textured soils (Simpson and Melsted, 1963). Ananthanarayana and Mithyantha (1970) stated that urease activity in dry and wetland soils was closely related to organic carbon content. Gould et al. (1973) determined a close correlation (r=0.99) between urease activity and organic carbon content. Vmax values obtained for soil urease activity were significantly correlated with organic carbon (r=0.99) and total nitrogen (r=0.99) contents (Tabatabai, 1973). In tropical soils from Trinidad (West Indies), the urease activity was significantly correlated with organic carbon content (Dalal, 1975a). In surface soils from Iowa, urease activity was significantly correlated with organic carbon (Tabatabai, 1977). Based on a significant

correlation recorded (r=-0.72***) between urease activity and organic carbon, Zantua et al., (1977) concluded that among the soil properties studied, organic matter has the greatest effect on urease activity. Beri et al. (1978) found that, in subtropical alkaline soils of India, urease activity was largely controlled by the organic carbon content, although the levels of organic carbon in these soils was very low. In ten Philippine wetland rice soils differing widely in pH, texture, and organic matter, multiple regression analysis showed that organic matter content of the soils accounted for most of the variation in soil urease activity and that the activity was significantly correlated (r = 0.89**) with organic carbon content (Sahrawat, 1980b). In acid soils of Sri Lanka, Wickremasinghe et al. (1981), observed no relationship between urea hydrolysis and organic carbon or texture. The application of organic matter in the form of *Sesbania aculeata* leaves increased the urea hydrolysis rates in non saline normal and saline - alkali soils (Bajpai et al., 1984). Application of decomposed organic matter increased urease activity in soils (Kumar and Wagnet, 1984). Marshall et al. (1990) reported high level of urease activity in organic horizons compared with the mineral horizons.

2.5.4 Soil Reaction (pH)

Simpson and Melsted (1963) marked pH only second to organic matter in the order of importance among the factors affecting urea hydrolysis in soils. In surface soils from

five great soil groups (Krasnozem, Chocolate, Yellow podzolic, Gley podzolic, and Redbrown earth) in Australia, McGarity and Myers (1967) reported a weak but positive correlation between soil reaction (pH 4.8 to 7.0) and urease activity. Skujins and McLaren (1969) obtained maximum urease activity between pH 6.5 and 7.0, in most of the soils that they examined. Urea hydrolysis occurred over a wide range of soil pH; urea hydrolysis being very slow below pH 4 and above pH 10, with the optimum rate attained at pH 8.0 (Delaune and Patrick, 1970). Dalal (1975a) reported that urease activity in toluene treated soils, was positively correlated with pH, but the correlation was not significant. Urease activity studies, using phosphate buffer, indicated, that the optimum reaction for soil urease activity was pH 8.8 (May and Douglas, 1976). Pettit et al. (1976) found that the urease activity was highest in soils at pH 6.5 with a broad plateau over a range of pH 5 to 8. Sahrawat (1983) did not observe any significant correlation between soil pH and urease activity in the Philippine wetland rice soils, with a pH range of 3.4 to 7.5. In Indian soils, Sinha and Prasad (1967) reported that urea hydrolysis was slow in acid soils of Bihar. However in very acid soils (pH 4.0-4.5) of Sri Lanka, Wickremasinghe et al. (1981) observed very high levels of urease activity. The hydrolysis of urea was also lower in high pH soils, with a high sodium carbonate content (Chandra and Abrol, 1972). Nitant (1974) reported that the highest urea hydrolysis rate was obtained in neutral soils (pH 7.4), followed by saline soil (pH 8.4) and the least in saline sodic soil (pH 10.1).

Beri et al. (1978) observed that urease activity decreased as the soil pH increased from neutrality and the correlation between urease activity and the soil pH was positive (r=0.50) but not significant. Maximum urease activity occurred at pH 7.3. Pal and Chhonkar (1979) reported that soil urease activity was highest between a pH range of 6.5 to 9.5, when the buffer method was used for assessing the urease activity. Though urease activity has been observed in soil having pH as low as 3.4 (Sahrawat 1983) and in soils with pH as high as 10.1 (Beri and Brar 1978), the optimum pH for urea hydrolysis appears to lie between 6.5 to 8.3 (Pettit et al., 1976; Beri et al., 1978).

2.5.5 Clay Content And Cation Exchange Capacity

Dalal (1975a) found that urease activity was significantly correlated with clay content, cation exchange capacity, and oxalate-extractable amorphous iron and aluminum. Urease activity of soils was correlated significantly with clay content (r=0.53*) and surface area (r=0.45*) and cation exchange capacity (r=0.67***) (Zantua et al., 1977). However, Beri and Brar (1978) and Pal and Chhonkar (1979) found that urease activity was not significantly correlated with clay content or cation exchange capacity of the soils. Dash et al. (1981) reported a positive correlation between urease activity and different particle size components (silt and clay) of the soils.

2.5.6 Total Soluble Salts and Salinity

Nitant (1974) reported that the rate of urea hydrolysis was low in saline and sodic soils. Gandhi and Paliwal (1976) observed that salinity reduced the urea hydrolysis rates in soils. Sankhayan and Shukla (1976) observed that the urea hydrolysis rate was slower in soils with high electrical conductivity. Dash et al. (1981) reported positive correlation between urease activity and specific conductance in surface soils from hills (r=0.65), pastures (r=0.56), and forests (r=0.68) in Orissa state (India). The average specific conductance was 0.13, 0.17 and 0.10 m. mhos cm^{-1} for the hill, pasture, and forest soils respectively. Bajpai et al. (1984) showed that urea hydrolysis was adversely affected by salinity in saline-alkali soils.

2.5.7. Bulk Density

Savant et al. (1987a) reported bulk density of soil could effect hydrolysis of broadcast urea and high bulk density increases urea hydrolysis.

2.6 UREA HYDROLYSIS: ASSAY TECHNIQUES

Most investigations have used estimation of ammonium nitrogen (Fisher and Parks, 1958; Stojanovic, 1959; Simpson and Melsted, 1963; Volk, 1966; McGarity and Myers, 1967; Paulson and Kurtz, 1969, 1970; Ananthanarayana and Mithyantha, 1970; Pancholy and Rice, 1973; Sahrawat, 1980b; Dash et al., 1981) or estimation of residual urea nitrogen remained

unhydrolysed (Overrein and Moe, 1967 Gould *et al.*, 1973; Dalal, 1975a; Sankhayan and Shukla, 1976; Zantua *et al.*, 1977; Beri and Brar, 1978; Pal and Chhonkar, 1979; Kumar and Wagnet, 1984; Sahrawat, 1984; Reynolds *et al.*, 1985 and others), to estimate urease activity in soils. Skujins and McLaren (1969) studied urea decomposition in soils by determining C-14 labelled CO_2 released through hydrolysis of C-14 labelled urea by soil urease. Assay techniques based on ammonium estimation can be in error if the ammonium produced is lost by volatilization or fixed by soil colloids.

Some workers have used different buffers to control soil pH during assays of urease activity. Skujins and McLaren (1969) used potassium acetate buffer (pH 5.5). Almost neutral pH (6.7 to 7.2) phosphate or citrate buffers were used by others (Stojanovic 1959; McGarity and Myers, 1967; Ananthanarayana and Mithyantha, 1970; May and Douglas, 1976). Pettit *et al.* (1976) studied urease activity in soils using Tris-HCl buffer (pH 7.0) and phosphate buffer (pH 7.0). Tabatabai and Bremner (1972) stated that use of THAM buffer (pH 9.0) is satisfactory for assay of urease activity in ammonium-fixing soils.

Many other research workers have not used any buffer to study urea hydrolysis in soils (Overrein and Moe 1967; Dalal 1975a; Zantua *et al.*, 1977; Sahrawat 1980a, 1984; Kumar and Wagnet, 1984).

In some studies, toluene was used with or without buffer to inhibit microbial activity (Conrad 1942a; Stojavanic, 1959; McGarity and Myers, 1967; Tabatabai and Bremner, 1972; Dalal 1975a; May and Douglas, 1976; Pal and Chhonkar, 1979; Dash *et al.*, 1981). Conrad (1942a), and Tabatabai and Bremner (1972) reported increased urease activity in soil samples to which toluene was added, whereas McGarity and Myers (1967) and Dalal (1975a) reported reduced urease activity in soil samples treated with toluene. Zantua and Bremner (1975a) did not find any difference in the urease activity of soil due to the addition of toluene. Based on the divergent opinions on the effect of addition of toluene on urease activity in soils, Bremner and Mulvaney (1978) concluded that addition of toluene to soil samples can cause a number of problems in assay of urease activity.

Among the procedures proposed to determine urease activity, the buffer method (Tabatabai and Bremner, 1972) and a non-buffer method (Zantua and Bremner, 1975) are commonly used. Bremner and Mulvaney (1978) stated that the buffer method detects urease activity that does not occur when soils are treated with urea in the absence of buffer; and that the non-buffer method provides a very good index of the ability of soils to hydrolyse urea under natural conditions and that the results are not influenced by the inclusion of toluene.

2.7 LABORATORY STUDIES

Many laboratory studies have been carried out under

optimum moisture and temperature conditions under varying periods of incubation (Simpson and Melsted, 1963; McGarity and Myers 1967; Ananthanarayana and Mithyantha, 1970; Dalal, 1975a; Beri and Brar, 1978; Sahrawat, 1980b; Vlek and Carter, 1983). In most studies, urea has been added in the form of solution to soil samples, but in some experiments urea was added to soils as solid. For example; chemically-pure crystalline urea was uniformly applied to the soil surface by Overrein and Moe (1967); Malhi and Nyborg (1979) spread urea evenly over the soil surface before incubation. Rachhpal-Singh and Nye (1984b) packed moist soils into columns and applied fine crystalline urea over the soil prior to incubation.

Wagnet et al. (1977) applied solution of urea enriched to 95 per cent N-15 in their experiments to study transformations of urea during leaching with soils packed in 15, 28, and 35 cm long columns. Campbell et al. (1984) used urea enriched with N-15; this was mixed with the soil, or branded prior to incubation.

2.7.1 Urea Hydrolysis Rates

To obtain comprehensive information about urea hydrolysis rates in surface soils, the data from some of the laboratory incubation studies conducted in different countries and in India are presented in Tables 1 and 2, respectively. Though information is available on urea hydrolysis rates in different soils, comparisons of urea hydrolysis rates must be

made with caution as different assay techniques have been used (Gould et al., 1986). The data presented in Table 1 shows that the urea hydrolysis rates ranged from 3.9 to 600 µg urea N hydrolysed g^{-1} soil h^{-1}.

Urea hydrolysis rates reported for Indian soils (Table 2) are generally low, when compared with the rates reported from other countries (Table 1). This could be due to the generally low organic carbon content of the Indian soils. In many studies, the moisture content of the soil varied from 40 per cent water holding capacity to field capacity (0.98 bar to 1/3 bar tension). Among the reports on urea hydrolysis rates in Indian soils, assayed with the non-buffer method, Saharawat (1984) reported the highest urea hydrolysis rate of 14.8 µg urea -N g^{-1} soil h^{-1}, for a Vertisol at ICRISAT Centre.

With reference to the number of reports by several workers that the rate of urea hydrolysis in soils treated with small amounts of urea was much slower than that observed with large amounts of urea, Bremner and Mulvaney (1978) observed that this could be due to urea added becoming a limiting factor in the assay procedure.

2.8 FIELD STUDIES

There are only few studies about urea hydrolysis under field conditions (Malhi and Nyborg, 1979; Aulakh and Rennie, 1984; Mohammed et al., 1984; McInnes et al., 1986). However, no studies report rates of urea hydrolysis. In all reports

Table 1: Laboratory studies: Urea hydrolysis rates of surface soils reported from different countries

Country	Soils	Organic carbon %	Soil pH	Incubation conditions		Method	Urea-N hydrolysis rate	Reference
				Moisture	Temperature °C		µg urea-N hydrolysed g^{-1} soil h^{-1}	
Australia	Pasture Sward	2.4	5.6		37	B(pH6.7)+T	56.9	McGority and Myers 1967
Australia	Diverse soils	2.5	6.6		37	B(pH8.8)+T	30.8	May and Douglas 1976
Ceylon	Acid Tea Soils	1.92	4.2	15-40%	22	N,B-T	3.8	Wickremasinghe et al 1982
Philippines	Wet land Rice soils	1.9	5.7	Waterlogged	30	NB-T	9.8	Sahrawat, 1983
Trinidad	Tropical diverse soils	4.2	5.1	50% WHC	37	NB-T	599.7	Dalal 1975a
						NB+T	341.6	Dalal 1975a
USA	Representing Illinois		6.0	60%	24		2.9	Simpson-Melsted 1963
USA	Alluvial Priarie	1.1	6.8	F.C	30		3.9	Delaune and Patrick 1970
							0.04	
USA	Diverse Iowa soils	2.6	6.4	FC	37	NB-T	18.2	Zantua et al 1977
USA	Diverse Utah and California soils	1.6	7.7	FC	37	NB-T	21.0	Kumar and Wagnet 1984
USA	Cultivated	1.4	6.4	Field Moist	28+1	NB-T	7.5	Reynolds et al 1985
	Pasture	3.04	6.10	Field Moist			15.9	

NB = Non Buffer method; B = Buffer method; +T = Toluene added; -T = Toluene not added;
FC = Field capacity; WHC = Water holding capacity

Table 2: Laboratory Studies: Urea hydrolysis rates of surface soils reported from different states in India.

Country	Soils	Organic carbon %	Soil pH	Incubation conditions		Method	Urea-N hydrolysis rate	Reference
				Moisture	Temperature °C		µg urea-N hydrolysed g^{-1} soil h^{-1}	
Andhra Pradesh	Alfisol	0.4	5.3	60% WHC	37	NB-T	5.1	Sahrawat, 1984.
	Vertisol	0.5	7.5		37		14.8	
Delhi	Clay loam	0.7	7.5	60% WHC	30	NB-T	3.6	Sahrawat, 1980.
	Sandy loam							
Haryana	Loamy sand	0.4	7.7	40% WHC	28±1		3.0	Sankhayan and Shukla 1976
	Sandy loam	0.6	8.0	FC	28±1	NB-T	2.4	Singh and Yadav 1981
	Sandy soil	0.2	7.5	FC	28±1		1.4	
Karnataka	Dry & Wet land	0.5	5.2		37	B(pH6.7)+T	26.1	Aanthanarayana and Mithyantha, 1970
	Red sandy loam	0.3	5.3	60% WHC	30	NB	0.1	Siddaramappa and Rao 1971
	Laterite	1.2	5.6				0.2	
	Black	0.7	8.1				0.1	
Orissa	Pasture	0.5		Field moist	32	B(pH9.0)+T	5.7	Dash et al 1981
	Forest	0.5					5.0	
	Mill	0.7					7.9	
Punjab	Alkaline soils	0.4	8.8	60%FC	37±1	NB-T	7.03	Beri and Brar 1978

NB = Non buffer method; B = Buffer method; +T = Toluene added; -T = Toluene not added;
FC = Field capacity; WHC = Water holding capacity

from field experiments (Table 3), the amount of urea -N hydrolysed was reported as the percentage "loss" of the urea - N applied. Also, the table shows that experimental conditions varied: there were different moisture and temperature regimes, different forms of urea applied, and different methods of urea application. It is difficult to compare urea hydrolysis rates, or draw conclusions on factors affecting urea hydrolysis in the field, based on these data as the influence of environmental factors and soil characteristics on urea hydrolysis were not studied in these experiments.

2.9 SIMULATION MODELS

Simulation models have been developed to understand urea transformation in soils (McLaren, 1970; Wagnet et al., 1977; Vlek and Carter, 1983; and Rachhpal-Singh and Nye 1984b). McLaren (1970) discussed a mathematical model to predict concentrations of urea-N NH_4^+ -N, and NO_3^- -N concentrations at different depths in soil columns. The conclusions were that intermediates such as NH_4^+ -N and NO_2^- -N reach maximal amounts as urea concentration declines, and, in the absence of denitrification NO_3^- -N acucmulates with depth. Although the model is general, it is limited to bare soils or to laboratory soil columns.

Wagnet et al. (1977) used a mathematical model to study the enzymatic hydrolysis of urea, nitrification, and denitrification in laboratory soil columns. The mathematical

Table 3: Urea hydrolysis data from field experiments

Country	Soils	Plot size	Moisture	Temperature °C	Form of urea used	Method of urea application	Quantity	Urea-N hydrolysed			Reference
								days	kg/ha	%	
Canada	Loam	6.8x1.8m	From 0.1	Mean 6	Urea	Mixed	56 kg N	14	53.2	95	Malhi and Nyborg 1979
	Loam		to 15.9 bar		pellets	Branded	56 kg N	14	49.3	88	
	Clay loam		tension		0.01 g	Mixed	56 kg N	14	53.2	95	
	Clay loam				weight	Branded	56 kg N	14	51.5	92	
	Silty clay loam					Mixed	56 kg N	14	49.3	88	
						Branded	56 kg N	14	41.4	74	
	Sandy					Mixed	56 kg N	14	53.8	96	
	Loam	Micro				Branded	56 kg N	14	52.6	94	
Canada	Dark brown	Plot		0-15	15N labelled						
	Chernozems	20 cm id 45 cm long	74 mm rainfall		Urea solution	Injected	100 kg N	21	60.0	60	Aulakh and Rennie 1984
New Zealand	Silt loam	Micro plot 0.44 m^2 rings 25 cm long	and 29 mm irrigation	17 (mean)	15 N labelled powdered urea	Sprinkled on surface	100 kg N	7	86.0	86	Mohammed et al 1984
USA	Silt loam Sandy loam	Micro plot 10 cm id 10 cm deep	After 94 mm rainfall	10-45	Urea solution	Injected	120 kg N	3	37.5	30	McInnes et al 1986

model was developed, on the assumption, that diffusion and mass transport are mechanisms of transport for urea, ammonium and nitrate; and that urea hydrolysis, ammonium oxidation and nitrate reduction processes follow first order reactions. The movement and transformation of urea, ammonium and nitrate in soil were mathematically described as a function of time and depth. Urea hydrolysis was found to be independent of initial concentration and the oxygen concentration of soil atmosphere. The usefulness of this model is that it can be used to study the nitrogen transformations in the laboratory.

Vlek and Carter (1983) studied problems associated with modelling urea hydrolysis as a part of an effort to model the behavior of urea by computer simulation. They studied hydrolysis of solution applied urea in different soils at various temperatures and moisture contents and fitted the disappearance of urea to zero and first order kinetic models. Their conclusions were that, for the purpose of simulation modelling, zero or first order rate equations are easier to handle than Michaelis-Menten equations and require the determination of fewer kinetic parameters. Full characterisation of the behavior of urea hydrolysis in soil is a pre-requisite to computer simulation model of urea nitrogen in soils.

Rachhpal-Singh and Nye (1984b) developed a mathematical model for predicting concentration profiles of urea, ammonium and soil pH in a soil column following diffusion from surface

application of urea. There was a good agreement between the observed and predicted concentration of urea, ammonium and soil pH values.

2.10 CONCLUSIONS

The review of literature on urea hydrolysis brings out the following salient points:

1. There are few data on urea hydrolysis rates in the field.

2. Field experiments have been rarely conducted specifically to determine urea hydrolysis rates, and the kinetics of urea hydrolysis have not been studied under field conditions.

3. There is no satisfactory data from field experiments to compare with the available information from laboratory incubation experiments.

4. The influence of important environmental variables such as moisture and temperature on urea hydrolysis rates in the field need to be studied, especially as divergent views have been expressed by many research workers based on laboratory studies (Bremner and Mulvaney 1978).

5. Future research work on urea fertilizer requires measurement of urea transformations in the field under agronomically realistic conditions (Gould et al., 1986).

MATERIALS AND METHODS

CHAPTER III

MATERIALS AND METHODS

Experimentation consisted of experiments to measure urea hydrolysis rates in the field, followed by laboratory incubations to determine whether urea hydrolysis rates could be predicted from the data built up from field and laboratory studies.

3.1. SOILS AND THEIR CHARACTERISTICS

The field experiments were conducted on an Alfisol and a Vertisol of the Patancheru and the Kasireddipalli series respectively, which are benchmark soils at ICRISAT Center. Subsequently, laboratory incubation studies were conducted on soil samples collected from the sites of the field experiments.

3.1.1. Alfisol

The Patancheru series is classified by Soil Taxonomy as a clayey-skeletal mixed Isohyperthermic family of Udic Rhodustalfs developed on weathered granite (Nagabhushana et al., 1987). The surface horizon of this soil, when uneroded, usually has a low clay content with the dominant clay mineral being a 1:1 type viz kaolinite. The increase in clay content with depth, in the B horizon, is a distinguishing feature of this soil, which is well drained and has a low water retention capacity. Other characteristics are a lack of water stable aggregation, low cation exchange capacity, and a slightly

acidic pH (El-Swaify et al., 1987).

3.1.2 Vertisol

The Kasireddipalli series is a fine montmorillonite isohyperthermic family of Typic Pellusterts. The soil is deep, has a high content of swelling (1:2) type clays, with montmorillonite as the dominant clay mineral, with a relatively high water retention capacity. The soil is calcareous and has a pH above 8. The soil is sticky with poor infiltration and impeded internal drainage while wet and excessively hard and difficult to work when dry (El Swaify et al., 1985).

Selected characteristics of the Alfisol and Vertisol are presented along with the results of the experiment at different sites.

More detailed description of the soils are given in the general description of all benchmark soils in India (Murthy et al., 1982).

3.2 EXPERIMENTAL

3.2.1 Field Experiment 1

The objective of this experiment was to study urea nitrogen transformations in the field for 72 hours after application of fertilizer urea to the surface of dry bare soils, followed by irrigation. This study was based on the suggestion of Sahrawat (1984) that on Vertisols, urea could be

applied to the soil surface at seeding before the onset of rains. In this experiment, urea was hand spread onto the soil surface and than washed into the topsoil by a light irrigation. Soil samples were collected at intervals for urea analysis to allow calculation of urea hydrolysis rates.

Soils:	Alfisol and Vertisol
Treatments :	0 and 100 kg N ha^{-1}
Replications:	4
Dates of experiment:	6-9 October, 1986
Duration of the experiment:	72 hours
Soil sampling intervals	2, 24 48 and 72 hours
Depth of soil sampling	0-15 and 15-30 cm

An area of 57.75m^2 (10.5 x 5.5 m) was located on the Alfisol and Vertisol sites and the surface of soils was made bare by removing vegetation and organic debris. At the Vertisol site, the bigger clods were broken with a wooden mallet. On the Alfisol the surface soils were lightly cultivated to a depth of 2.5 cm with a hand hoe to breakup the surface crust. Individual plots of 4 m^2 (2 x 2 m) were marked out leaving a space of 0.5 m between the individual plots (Fig.1). For the nitrogen treatment, solid dry crystalline urea was handspread onto the surface of the dry soil at the rate of 86.96 g per plot, so as to add 100 kg N ha^{-1}. After the application of urea, 80 litres of water was added to each plot by a water can. In both soils, the 0 N and 100 N plots received equal quantity of water. Each plot was then divided into 4 sub-

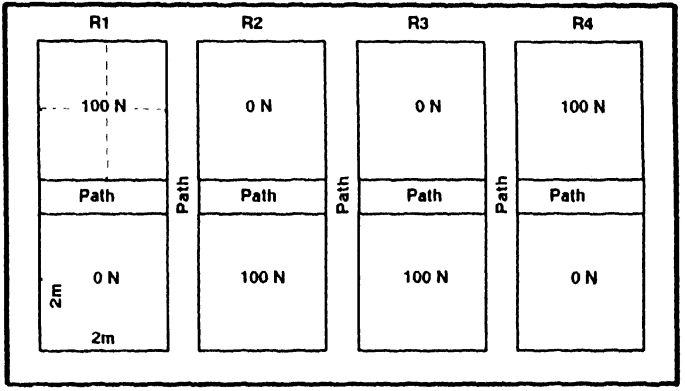


Figure 1. Exp.1: Layout of the field plots
Dotted lines indicate the sub-plots in a treatment.

plots for sampling at 4 times. The treatments in each replication, and sites for the time series sampling within the sub-plots, were randomised. Soil samples were collected from the 0-15 and 15-30 cm depths at intervals of 2, 24, 48 and 72 hours after urea application with a 5 cm (i.d.) "Stace-Palm" modification of the Veihemeyer soil coreing tube" and approximately 300-400 g of composite soil samples were collected and placed into polyethylene bags. The composite soil sample represents soil from 3 individual samples. Accurately weighed field moist samples of 10-12 g were extracted with 100 ml of 2 M KCl containing phenyl mercuric acetate and residual urea, ammonium, nitrite, and nitrate nitrogen in the extracts were determined. Moisture content of the soil samples was determined by drying the soil samples at 105^{o}C for 48 hours.

3.2.2 Field Experiment 2

This experiment was based on the general practice of urea application to a wet soil soon after rains, under rainfed farming systems. The objective was to study urea hydrolysis on application of solid urea fertilizer to a wet soil. (A probable ambience of a soil 12-24 hours after receiving a good soil soaking rain).

Soils	:	Alfisol and Vertisol
Treatments	:	0, 50 and 100 kg N ha^{-1}
Source of nitrogen	:	Urea
Replications	:	4
Dates of experiment	:	17-22 December 1986
Soil sampling intervals	:	2, 24, 48, 72, 96, 120 and 144 hours

Depth of soil sampling: 0-15 and 15-30 cm

On the Alfisol and Vertisol a 84 m^2 (10.5 x 8 m) area was marked out, and surface area cleared by removing vegetation and organic debris with a hand hoe. The entire site was bunded and 800 litres of water was applied ensuring wetting of the entire marked area. After 18 hours plots of 4 m^2 (2 x 2 m) were marked 0.5 m away from the border leaving a distance of 0.5 m between replications and also treatment plots. Urea was applied at the rates of 43.48 and 86.86 g per 4 m^2 plot so as to apply 50 and 100 kg N ha^{-1} respectively. Urea was sprinkled on wet soil after working up the soil with a hand hoe up to 2-5 cm deep. Each treatment plot was divided into 8 subplots for each subsequent sampling time. The treatments in each replication and the location of the time series samplings were randomised. Soil samples were drawn from 0-15 and 15-30 cm depth at intervals of 2, 24, 48, 72, 96, 120 and 144 hours after urea application, for analysis.

The procedure described in the first experiment was followed for the collection of soil samples, extraction with 2MKCl containing phenyl mercuric acetate, determination of

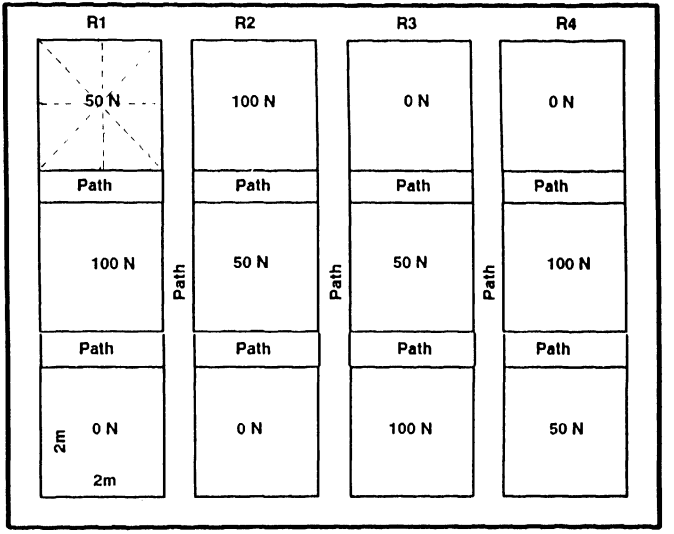


Figure 2. Exp.2: Layout of the field plots
Dotted lines indicate the sub-plots in a treatment.

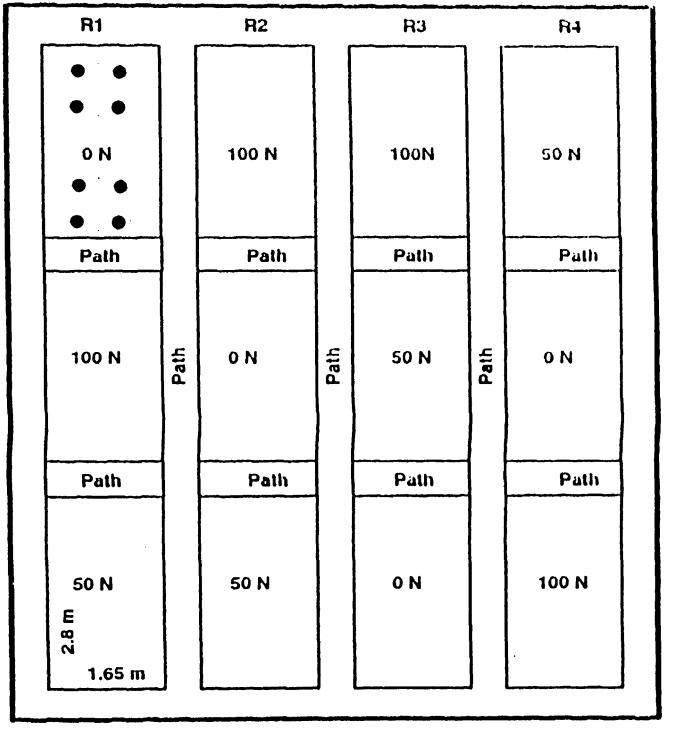


Figure 3. Exp.3. Layout of the microplots(●).

nitrogen and soil moisture determination.

3.2.3 Field Experiment 3

The results of the two previous field experiments have showed that urea hydrolysis rates were slow. Also, the soil moisture content decreased rapidly during the course of hydrolysis of urea especially on the Alfisol, and the recovery of inorganic form of nitrogen following urea hydrolysis was low in Experiment 1. Therefore, it was planned to study urea hydrolysis under a more uniform soil moisture status and using microplots in the field.

In this experiment, the soil was throughly irrigated to bring it to near field capacity. Then urea in solution was mixed with the 0-5 cm depth of soil in small microplots which were covered with polyethylene sheets. The purpose of studying urea hydrolysis using the covered microplots was to reduce loss of soil moisture through evaporation and to bring intimate contact between soil and urea, and to minimise the sampling error.

Soils	:	Alfisol and Vertisol
Treatments	:	0, 50 and 100 kg N ha^{-1}
Source of nitrogen	:	Urea
Replications	:	4
Dates of experiment	:	24-31 October 1987 (Alfisol) 23-30 October 1987 (Vertisol)
Duration of the experiment	:	168 hours
Soil sampling intervals	:	0, 24, 48, 72, 96, 120, 144, and 168 hours
Depth of soil sampling	:	0-5 and 5-10 cm.

An area of 115.4 m^2 (11.4 m x 10.1 m) was marked on Alfisol and Vertisol and vegetation and organic debris were removed from surface. The Vertisol was ploughed once, and after breaking the clods, it was worked with a rake to level the soil. Plots of 4.62 m^2 (2.8 m x 1.65 m) were marked 1m away from the border in such a manner that each replication had 3 treatment plots. The distance between individual plots was 0.5 m. All the treatment plots were bunded, and water was applied in each plot at the rate of 100 litres per plot for five consecutive days between 19-23 October on the Alfisol and 18-22 October 1987 on the Vertisol. On the sixth day, microplots of 38.5 cm^2 were established by pushing 12 cm long polyvinyl chloride (PVC) tubes, with an inner diameter of 7 cm, to a depth of 10 cm into the moist soil, leaving 2 cm of the tube above the soil surface. Eight such microplots were established in each treatment plot, one for each of the 8 sampling periods. The polyvinyl chloride tubes were marked at 2 cm and 7 cm length from the tip so that soil samples from 0-5 cm and 5-10 cm could be collected separately after removal of the tube from the plot. All the treatments in a replication and the periods of sampling in each plot were randomised.

Urea in solution was added to soil in the microplot. The urea solution was prepared by dissolving 8.37 g chemically pure crystalline urea in 1000 ml distilled water. This urea solution was mixed with the soil from 0-5 cm depth of the microplot in the following manner.

Treatment	Urea solution (ml)	Water (ml)
0 N	0	10
50 N	5	5
100 N	10	0

Soil upto 5 cm depth was taken out from the microplot and put into a plastic container. Urea solution and water were added to the soil while rotating the plastic container fixed to a hand operated rotary device. The soil was returned to the microplot after mixing urea solution with the soil. The entire operation of removing the soil from an individual microplot, mixing with urea solution and returning the soil to the microplot was done within 2 minutes. The treatment plots were then covered with polyethylene sheets. At the time of sampling, the appropriate microplot tube was removed, and the 0-5 and 5-10 cm depth soil samples were separated.

From each depth about 50 g accurately-weighed field-moist sub-samples were extracted with 150 ml of 3.5 M KCl containing phenyl mercuric acetate, immediately after removal of the samples at the experimental site. The high concentration of KCl used (3.5 M) in this experiment was chosen to reduce the volume of extractant, while maintaining the K^+ concentration of 10 to 20 milli equivalents g^{-1} soil required for complete extraction of $NH4^+$ ion from the soil (Sahrawat, 1979). Soil pH and moisture content of the samples were also determined. Soil temperatures were recorded at 0-5 and 5-10 cm depth, at the time of soil sample collection and in the afternoon.

3.2.4 Field Experiment 4

In the previous experiment using microplots, it was observed that nearly 90 per cent of urea nitrogen applied has hydrolysed within 24 hours. To confirm this observation urea hydrolysis was studied over the first 24 hours using microplots, but urea hydrolysis was examined over much shorter time intervals than in the earlier experiment to provide a better estimation of the rate of hydrolysis. Also, the temperature changes in the microplots were observed every 4 hours.

Soils	:	Alfisol and Vertisol
Treatments	:	0, 50 and 100 N kg ha^{-1}
Source of nitrogen	:	Urea
Replications	:	4
Dates of experiment	:	27 Feb - 28 February 1988 (Alfisol) 19-20 March (Vertisol)
Duration of the experiment	:	24 hours
Soil sampling intervals	:	0, 4, 8, 12, 16, 20, and 24 hours

Microplots in Alfisol and Vertisol were set up in the manner described in Experiment 3, except that each treatment plot received 200 litres of water per day for seven days prior to establishment of microplots. Soils were sampled at 0, 4, 8, 12, 16, 20, and 24 hours, after urea application. Mixing soil with urea solution, soil sample collection, and preparation of KCl extracts were done as described in Experiment 3.

3.2.5 Laboratory Incubation Experiment

Incubation studies were carried out on urea nitrogen transformation over a 24 hour period so as to provide the data for comparing with those from the microplot experiments. In this study also urea was added to the soil samples in the form of solution, and urea hydrolysis was determined at 4 hour intervals.

Soil samples from the 0-5 cm depth of RW 3 (Alfisol) and BW 6 (Vertisol) plots were air dried, ground, and passed through a 2 mm seive. Subsamples of 10 g of air dry soil was weighed into Nalgene shaking bottles. To the soil samples from Alfisol, 1 ml of urea solution containing 666 µg urea nitrogen was added, which in the field is equivalent to 50 kg N ha^{-1}, similarly 2 ml of urea solution was added to another set of soil samples to give 1332 µg N which is equivalent to 100 kg N ha^{-1}. To the soil samples from the Vertisol, urea solution containing 970 µg N and 1940 µg N was added so as to give 50 and 100 kg N ha^{-1} respectively. After the addition of urea solution, the moisture content of the sample was adjusted to field capacity for the Alfisol (24 per cent W/W) and Vertisol (40 per cent W/W) (Sahrawat 1984). The soil samples were incubated at 32°C. After 0, 4, 8, 12, 16, 20 and 24 hours of incubation, bottles were removed and the soil was extracted with 100 ml of 2 M KCl containing phenyl mercuric acetate. The soil samples of '0' hour were not incubated but were extracted with 2 M KCl immediately after the addition of urea

solution and water required for moisture adjustment. The KCl extracts were analysed for residual urea, ammonium, nitrite and nitrate nitrogen forms.

3.3 METHODS OF SOIL ANALYSIS

3.3.1 Characteristics of soils

The following soil characteristics were determined in soil samples from experimental plots. The size distribution of particles was determined by using the hydrometer method (Gee and Bauder, 1986), and bulk density by core method (Blake and Hartge, 1982). The moisture content of soil samples was determined by the gravimetric method with oven drying (Gardner, 1982). The pH of soil samples was determined using a glass electrode with a 1:2 soil: water ratio (Jackson 1967) and cation exchange capacity of soils was measured by the sodium saturation method of Bower *et al*. (1952). The organic carbon content of the soils was determined by the rapid titration method suggested by Walkley and Black (1934).

3.3.2 Analysis of KCl Extracts

Urea nitrogen in KCl extracts was determined by the modified diacetyl monoxime method (Bremner 1982). Exchangeable ammonium and nitrate forms of nitrogen were estimated by steam distillation method and nitrite nitrogen by modified Greiss-Ilosvay method (Keeney and Nelson 1982).

3.4. PRESENTATION OF EXPERIMENTAL DATA

3.4.1 Characteristics of soils

The general characteristics of experimental soils are presented in Tables 4, 8, and 12 along with the results.

3.4.2 Urea Nitrogen Hydrolysed

In the field experiments 1 and 2 urea nitrogen hydrolysed was computed from the difference between urea nitrogen applied and the urea nitrogen recovered in soil samples collected at different sampling intervals. In the field microplot experiments 3, and 4 and in the incubation studies the decrease of urea nitrogen in soil samples analysed at zero hour sampling time was considered as urea nitrogen hydrolysed.

3.4.3 Kinetics of Urea Hydrolysis

Urea hydrolysis kinetics were studied by using regression methods. The non-linear least- squares method of Gauss-Newton was used (Hartley, 1961). The predicted values of urea hydrolysed (Y) to fit in zero and first order reactions was determined from the observed values of residual urea nitrogen in soils. To determine predicted value (y) for a zero order, relationship the model $Y = a - bx$ was used, and for a first order relationship the model used was $y = ae^{-bt}$.

In these two models a is intercept, b is coefficient of regression, and x and t are time intervals. In the zero order reaction the coefficient of regression b is K_o and in the first order reaction it is K_1.

3.4.4 Statistical Analysis

The moisture content (per cent), urea, ammonium, nitrite, and nitrate nitrogen contents were statistically analysed using a split - split plot method of analysis. The analysis of variance was done using GENSTAT Statistical Analysis package under the VMS operating system on a MICROVAX-3900 computer available at ICRISAT Center.

RESULTS

CHAPTER IV

RESULTS

4.1 FIELD AND LABORATORY EXPERIMENTS

The data on urea movement into the soil, its hydrolysis, kinetics of urea hydrolysis, and accumulation of inorganic-N following urea hydrolysis in the Alfisol and Vertisol are presented separately for each field and laboratory experiments. Soil characteristics of experimental plots are presented in Tables 4, 8 and 12 along with the results.

4.1.1 Field experiment 1. Application of Solid Urea to Dry Soil, Followed by Irrigation

4.1.1.1 Urea Hydrolysis

The data on urea recovered from the 0-15 and 15-30 cm depths of the Alfisol and the Vertisol are given in Tables 5 and 6. In the Alfisol urea was recovered only from the 0-15 cm depth. In the Vertisol, almost all urea was recovered from the 0-15 cm depth and only 0.9 mg urea N kg^{-1} soil out of 58 mg urea-N applied was recovered from the 15-30 cm depth. Based on the urea recovered after 72 hours (Tables 5 and 6), 84 per cent of applied urea was hydrolysed in the Alfisol and 82 per cent in the Vertisol.

4.1.1.2 Kinetics of Urea Hydrolysis

In both the Alfisol and the Vertisol, urea hydrolysis fitted the relationship for a first order reaction better than that for a zero order reaction (Figure 4). In the Alfisol,

however the data also gave a good fit to a zero order relationship. Urea hydrolysis was faster in the Vertisol than in the Alfisol. From the first order reaction about 2.4 per cent and 3.6 per cent of urea-N in the Alfisol and the Vertisol was hydrolysed per hour.

4.1.1.3 Effects of Environmental Factors

Figure 5 shows that moisture content of the surface soil in both the Alfisol and the Vertisol decreased with time. In the Alfisol, the decrease was very substantial, most of it occurring in the first day - the decrease being 16.7 per cent in the 0-15 cm depth and 12.4 per cent W/W in the 15-30 cm depth between 2 and 24 hours after urea application. In the next two days, the moisture content decreased by only 1-2 per cent. Urea hydrolysis was rapid while moisture content was decreasing from 22.2 to 3.5 per cent during the first 48 hours. In the Vertisol the change in the moisture content was more gradual and the initial decrease in the 0-15 cm depth was accompanied by an increase in the 15-30 cm depth presumably due to drainage. The maximum urea hydrolysis occurred during the first 24 hours, when the moisture content of the 0-15 cm depth decreased from 23 to 19.5 per cent.

A mean maximum soil temperature of 31.9 ^{o}C was recorded at 1417 hours during the experimental period (Table 7). The weather data (Appendix C) shows that the daily mean minimum and maximum air temperatures were 19.5^{o}C and 33.3^{o}C during the conduct of the experiment.

4.1.1.4 Urea Hydrolysis Products

The changes in NH_4^+-N, NO_2^--N and NO_3^--N concentrations in the Alfisol and the Vertisol are shown in Figures 6 and 7 respectively. In both soils a decrease in urea-N was accompanied by an increase in NH_4^+-N with a very small accumulation of NO_3^--N and only trace amounts of NO_2^--N.

In the Alfisol, 56 per cent of urea nitrogen hydrolysed was recovered as inorganic-N (NH_4^+-N, NO_2^--N and NO_3^--N), with NH_4^+-N accounting for 93 per cent of the recovered-N (Appendix A). In the Vertisol 58 per cent of urea-N hydrolysed was recovered as total inorganic-N and 97 per cent of it was NH_4^+N (Appendix B). A greater amount of urea was hydrolysed in the Alfisol than in the Vertisol.

Table 4: Characteristics of the experimental soils:

	Alfisol*		Vertisol*	
Depth(cm)	0-15	15-30	0-15	15-30
Organic carbon %	0.35	0.27	0.60	0.41
Total nitrogen %	0.06	0.05	0.06	0.06
Ammonium N (mg kg^{-1} soil)	10.7	6.7	18.9	15.9
Nitrate-N (mg kg^{-1} soil)	2.4	2.8	13.9	13.4
pH (1:2 H_2O)	5.8	5.7	8.4	8.5
Sand fraction %	71.6	63.1	33.3	27.3
Silt %	8.0	9.3	15.1	19.4
Clay %	20.4	27.6	52.6	53.3
CEC C mole kg^{-1} soil	9.4	8.8	36.5	29.5
Bulk density g/cc	1.31	1.36	1.15	1.30

* Location in ICRISAT: Alfisol : Field R C E 1
Vertisol: Field B W 4

Table 5. Experiment 1: Transformations of urea nitrogen in an Alfisol in the field: urea, ammonium, nitrite and nitrate-N concentrations (mg N kg^{-1} soil) in unamended and amended soil[a]

Forms of nitrogen	Soil depth cm	Urea-N added kg/ha^{-1}	Time (h) 2	24	48	72	SE
Urea-N	0-15	100	46.6	32.3	13.6	7.9	
		0	0	0	0	0	
							±0.59
	15-30	100	0	0	0	0	
		0	0	0	0	0	
NH_4^+-N	0-15	100	4.0	13.7	20.6	24.9	
		0	2.9	2.4	3.2	2.3	
							±0.67
	15-30	100	2.2	2.1	2.0	1.3	
		0	1.9	2.0	2.0	1.4	
NO_2^--N	0-15	100	0.06	0.08	0.03	0.07	
		0	0.05	0.06	0.02	0.03	
							±0.02
	15-30	100	0.04	0.03	0.03	0.02	
		0	0.02	0.03	0.01	0	
NO_3^--N	0-15	100	2.6	2.8	3.4	3.7	
		0	3.1	3.0	2.4	2.1	
							±0.36
	15-30	100	1.5	1.4	1.3	1.2	
		0	1.0	1.2	1.2	1.3	

[a] Solid urea was added to the dry surface of soil

Table 6. Experiment 1: Transformations of urea nitrogen in a Vertisol in the field: urea, ammonium, nitrite and nitrate-N concentrations (mg N kg^{-1} soil) in unamended and amended soil[a]

Forms of nitrogen	Soil depth cm	Urea-N added kg ha-1	Time (h) 2	24	48	72	SE
Urea-N	0-15	100	48.7	18.2	12.4	10.2	
		0	0	0	0	0	
							±0.57
	15-30	100	0	0	0.9	0	
		0	0	0	0	0	
NH_4^+-N	0-15	100	7.1	25.7	28.6	30.0	
		0	3.7	3.5	3.3	3.0	
							±0.55
	15-30	100	2.9	2.8	2.2	1.7	
		0	2.7	2.1	1.8	1.8	
NO_2^--N	0-15	100	0.07	0.07	0.12	0.10	
		0	0.07	0.06	0.05	0.08	
							±0.0
	15-30	100	0.03	0.06	0.05	0.02	
		0	0.04	0.07	0.04	0.01	
NO_3^--N	0-15	100	9.4	10.9	11.0	10.6	
		0	9.7	9.2	9.2	9.2	
							±0.9
	15-30	100	5.3	5.8	6.0	5.9	
		0	5.1	4.7	5.9	6.3	

[a] Solid urea was added to the dry surface of soil

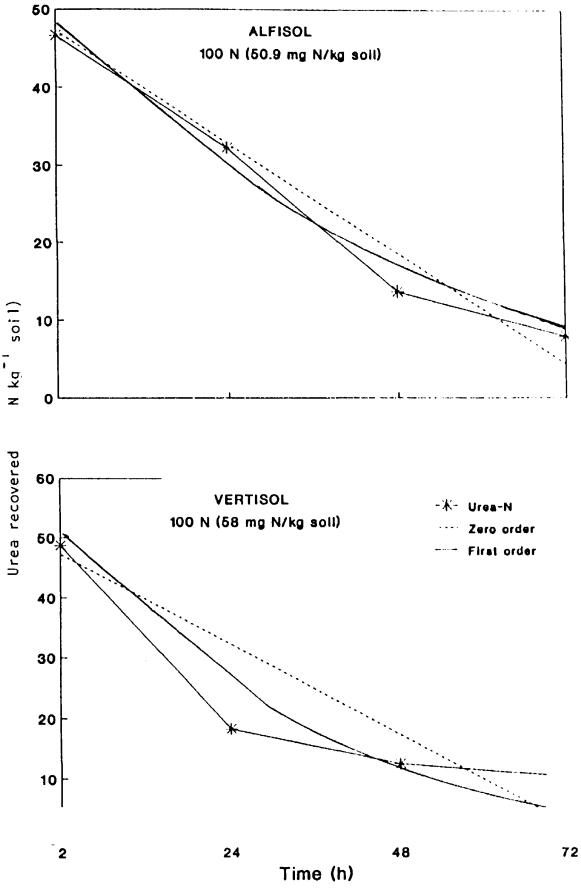


Figure 4: Exp.1: Field disappearance of urea-N from 0-15 cm, after application of 100 kg N ha^{-1} as urea. The zero and first order relationships are:

Alfisol:	Zero order	$Y = 48.1 - 0.61x$	$R^2 = 0.95$
	First order	$Y = 50.6e^{-0.024t}$	$R^2 = 0.99$
Vertisol:	Zero order	$Y = 48.2 - 0.64x$	$R^2 = 0.73$
	First order	$Y = 54.7e^{-0.036t}$	$R^2 = 0.98$

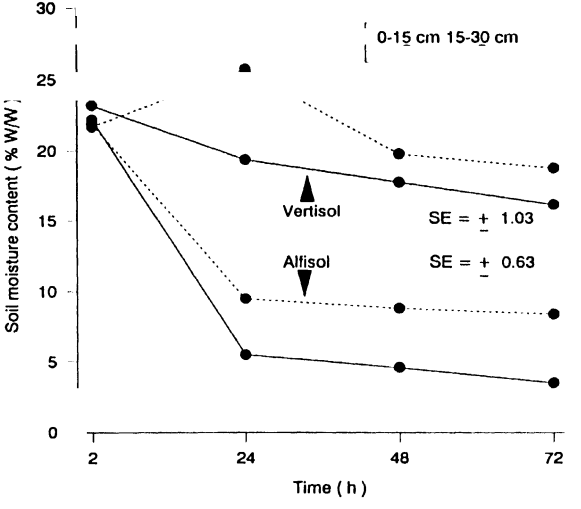


Figure.5 Exp.1: Soil moisture contents in 0-15 and 15-30 cm depths.

Table 7. Experiment I: Soil temperatures (°C) recorded at ICRISAT meterology observatory* during the conduct of Experiment 1, 17-20 October 1986.

Soil depth	Recording time (h)	Dates				Mean
		17	18	19	20	
0-15 cm	0717	30.0	30.0	29.5	28.1	29.4
	1417	32.5	32.4	31.8	31.0	31.8

* Vertisol

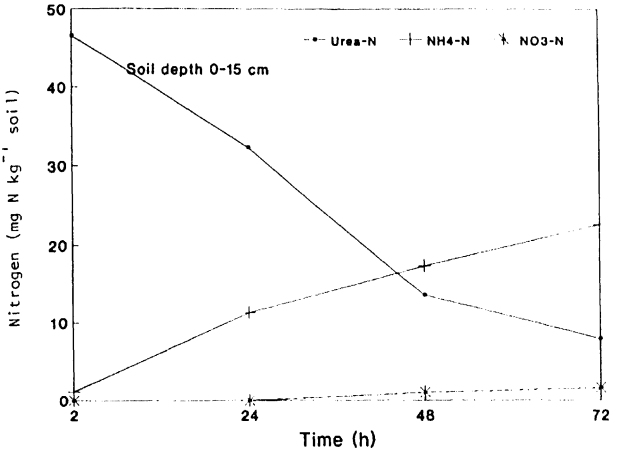


Figure 6: Exp.1: Urea derived inorganic nitrogen in the Alfisol after application of 100 kg N ha^{-1}.

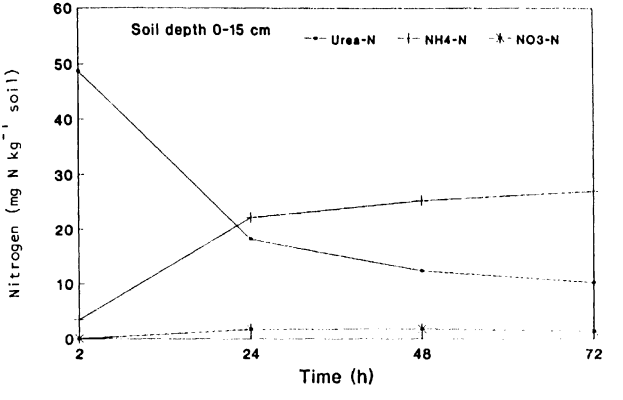


Figure 7: Exp.1: Urea derived inorganic nitrogen in the Vertisol after application of 100 kg N ha^{-1}.

4.1.2 Field experiment 2: Application of solid urea to a moist surface soil

4.1.2.1 Urea Hydrolysis

The urea recovered in the Alfisol and the Vertisol are given in Tables 9 and 10. As in the first experiment, when urea was applied to dry soil, almost all the urea remained in the 0-15 cm depth, and only trace amounts moved beyond the 15 cm depth. The urea recovered in the two soils 144 hours after urea application indicates that urea hydrolysis was slower in the Alfisol than in the Vertisol. In the Alfisol (Table 9), 77 per cent and 81 per cent of the applied urea was hydrolysed in the 50 and 100 N treatments; and, in the same treatments for the Vertisol, 97 per cent and 95 per cent of the urea was hydrolysed.

4.1.2.2 Kinetics of Urea Hydrolysis

In both the 50 and 100 N treatments urea hydrolysis fitted first order reaction kinetics more closely than zero order reaction kinetics in both the Alfisol (Figure 8) and the Vertisol (Figure 9). However, in the Alfisol the differences in R^2 values of the zero and the first order reactions were only 0.06 and 0.04 in the 50 and 100 N treatments, but they were much larger (0.15) for both treatments in the Vertisol. The first order reaction relationship shows that in the Alfisol urea-N hydrolysis was 0.9 per cent and 1.1 per cent per hour in the 50 and 100 N treatments. In the Vertisol, urea-N hydrolysis was 2.2 per cent per hour in the two treatments. Urea hydrolysis was therefore twice as rapid in the Vertisol than in the Alfisol.

4.1.2.3 Effects of Environmental Factors

Changes in soil moisture with time in the Alfisol and the Vertisol are shown in Figure 10. In the Alfisol the decrease in moisture content between 2-144 hours was 4.7 per cent and 3.5 per cent in the 0-15 and 15-30 cm depths. Maximum urea hydrolysis occurred while soil moisture decreased markedly from 9 to 6 per cent in the 0-15 cm depth, between 2-72 hours, in the 50 and 100 N treatments. In the Vertisol, soil moisture decreased by 5 per cent in the 0-15 cm depth and by 4 per cent in the 15-30 cm depth between 2-144 hours. Urea hydrolysis was maximum in the 0-15 cm depth when moisture content was decreasing from 23 to 20 per cent between 2-72 hours in the two treatments.

The mean soil temperature recorded at 1417 hours each day during the experimental period was 27.3 ^{o}C (Table 12). The average minimum and maximum air temperatures were 15.8^{o}C and 29.2^{o}C (Appendix H).

4.1.2.4 Urea Hydrolysis Products

In the Alfisol, a greater part of the hydrolysed urea was recovered as NH_4^+-N in the 0-15 cm depth (Figures 11 and 12). Ammonium-N increased steadily with time throughout the 144 hour measurement period. However, only a small proportion of the accumulated NH_4^+-N was converted to NO_3^--N, the increase in NO_3^--N being less than 5 mg N kg^{-1} soil. There was only a little change in the NO_3^--N below the 15 cm depth. In the Vertisol, NH_4^+-N reached a peak 96 hours after urea application in both the 50 and 100 N treatments. As NH_4^+-N

content decreased, NO_3^--N increased markedly (Figures 13 and 14). In the 0-15 cm depth of the 50 N treatment (Figure 13) NO_3^--N was almost same as that of NH_4^+-N at about 144 hours and also there was a sharp increase of NO_3^--N below the 15 cm soil depth, reflecting some downward movement of NO_3^- -N. In the 100 N treatment (Figure 14) also there was an increase in NO_3^-N after 96 hours in the two depths.

In the Alfisol, 91 per cent of the urea-N hydrolysed was recovered as inorganic nitrogen in the 50 N treatment; of the recovered mineral or inorganic nitrogen, 81 per cent was NH_4^+ N and 18 per cent as NO_3^--N (Appendix D). In the 100 N treatment 86 per cent of urea-N hydrolysed was recovered as inorganic-N (Appendix E), with 82 per cent of it as NH_4^+-N and 17 per cent as NO_3^--N. In the Vertisol, the recovery of urea-N hydrolysed as inorganic nitrogen was only 78 per cent in the 50N treatment. Nitrate-N (55 per cent) was greater than NH_4^+-N (45 per cent) (Appendix F). The total inorganic-N recovered following urea hydrolysis was 79 per cent in the 100 N treatment with 67 per cent of it as NH_4^+-N and 33 per cent as NO_3^--N (Appendix F). More inorganic-N was recovered from the Alfisol than in Vertisol though more urea was hydrolysed in the Vertisol.

Table 8: Characteristics of the experimental soils

	Alfisol*		Vertisol*	
Depth(cm)	0-15	15-30	0-15	15-30
Organic carbon %	0.28	0.19	0.42	0.38
Total nitrogen %	0.04	0.04	0.06	0.06
Ammonium-N (mg kg^{-1} soil)	9.6	8.6	17.5	15.3
Nitrate-N (mg kg^{-1} soil)	8.0	7.2	11.8	10.3
pH (1:2 H_2O)	5.3	5.8	8.3	8.4
Sand fraction %	83.4	82.1	25.5	23.5
Silt %	5.0	3.9	22.0	23.5
Clay %	11.6	14.0	51.3	53.0
CEC C mole kg^{-1} soil	5.9	4.9	30.5	27.5
Bulk density g/cc	1.6	1.64	1.10	1.21

*Location in ICRISAT: Alfisol : Field RW 3
Vertisol: Field BW 6

Table 9. Experiment 2: Transformations of urea nitrogen in an Alfisol in the field: urea, ammonium, nitrite and nitrate-N concentrations (mg N kg^{-1} soil) in unamended and amended soil[a]

Forms of nitrogen	Soil depth cm	Urea-N added kg/ha^{-1}	Time (h) 2	24	48	72	96	120	144	SE
Urea-N	0-15	100	38.7	31.0	28.6	17.5	13.8	10.6	7.8	
		50	18.3	15.3	11.8	10.4	9.1	6.8	4.8	
		0	0	0	0	0	0	0	0	
										±0.64
	15-30	100	0	0.3	0	0	0	0	0	
		50	0	0	0	0	0	0	0	
		0	0	0	0	0	0	0	0	
NH_4^+-N	0-15	100	5.0	8.4	10.6	18.3	19.8	21.3	25.3	
		50	4.1	5.0	7.7	10.1	11.3	11.0	13.3	
		0	3.3	3.0	2.4	2.8	2.7	2.3	1.7	
										±0.32
	15-30	100	1.6	1.7	1.7	1.6	2.0	1.5	1.6	
		50	1.7	1.9	1.7	1.8	1.9	1.9	1.6	
		0	2.1	1.8	1.7	1.9	1.6	1.4	1.4	
NO_2^--N	0-15	100	0.04	0.02	0.08	0.08	0.06	0.08	0.09	
		50	0.01	0.01	0.02	0.06	0.03	0.06	0.03	
		0	0.01	0	0	0.03	0.01	0.01	0.02	
										±0.01
	15-30	100	0.03	0	0.04	0.07	0.16	0.15	0.26	
		50	0	0	0.03	0.03	0.08	0.05	0.03	
		0	0	0.02	0	0.02	0.04	0.03	0.03	
NO_3^--N	0-15	100	3.0	2.9	3.6	3.3	3.7	5.8	8.3	
		50	2.6	3.0	3.0	3.1	3.7	4.7	6.4	
		0	2.8	2.8	2.5	2.7	2.9	3.0	4.1	
										±0.26
	15-30	100	2.6	2.3	2.6	1.9	2.6	2.9	3.1	
		50	2.0	1.9	2.1	2.3	2.7	2.7	2.7	
		0	2.5	2.2	2.4	2.0	2.1	2.2	2.4	

[a] Solid urea was added to the surface of wet soil

Table 10. Experiment 2: Transformations of urea nitrogen in a Vertisol in the field: urea, ammonium, nitrite and nitrate-N concentrations (mg N kg^{-1} soil) in unamended and amended soil[a]

Forms of nitrogen	Soil depth cm	Urea-N added kg/ha^{-1}	Time (h) 2	24	48	72	96	120	144	SE
Urea-N	0-15	100	51.7	31.6	20.4	15.1	4.9	4.0	2.8	
		50	23.6	14.6	11.2	5.1	4.2	1.0	0.9	
		0	0	0	0	0	0	0	0	
										±1.4
	15-30	100	0	0	0	0	0	0	0	
		50	0	0	0	0	0	0	0	
		0	0	0	0	0	0	0	0	
NH_4^+-N	0-15	100	7.5	18.1	24.6	32.4	42.2	35.9	32.7	
		50	5.8	8.9	11.8	17.0	19.7	16.1	12.3	
		0	3.0	2.9	2.7	2.7	2.7	2.5	2.4	
										±0.61
	15-30	100	2.8	2.7	2.6	3.2	2.8	2.9	2.8	
		50	2.9	3.0	2.8	2.8	2.7	2.8	2.8	
		0	3.0	2.9	2.8	2.7	2.6	2.6	2.5	
NO_2^--N	0-15	100	0.05	0.06	0.11	0.11	0.18	0.16	3.34	
		50	0.03	0.03	0.08	0.12	0.16	0.07	0.18	
		0	0.07	0.05	0.03	0.05	0.06	0.10	0.10	
										±0.03
	15-30	100	0.06	0.07	0.07	0.07	0.05	0.11	0.03	
		50	0.04	0.06	0.06	0.12	0.02	0.04	0	
		0	0.07	0.02	0.05	0.06	0.03	0.08	0.08	
NO_3^--N	0-15	100	10.1	8.5	10.1	10.1	10.0	18.2	22.1	
		50	9.0	8.4	8.4	9.9	9.5	15.0	19.7	
		0	9.9	8.5	8.7	9.0	9.4	14.0	10.3	
										±0.89
	15-30	100	8.7	8.8	9.9	9.2	10.3	10.3	11.5	
		50	8.6	8.9	8.9	8.7	8.5	10.1	11.5	
		0	8.2	8.3	8.7	8.3	8.6	8.1	8.5	

[a] Solid urea was added to the wet surface of soil

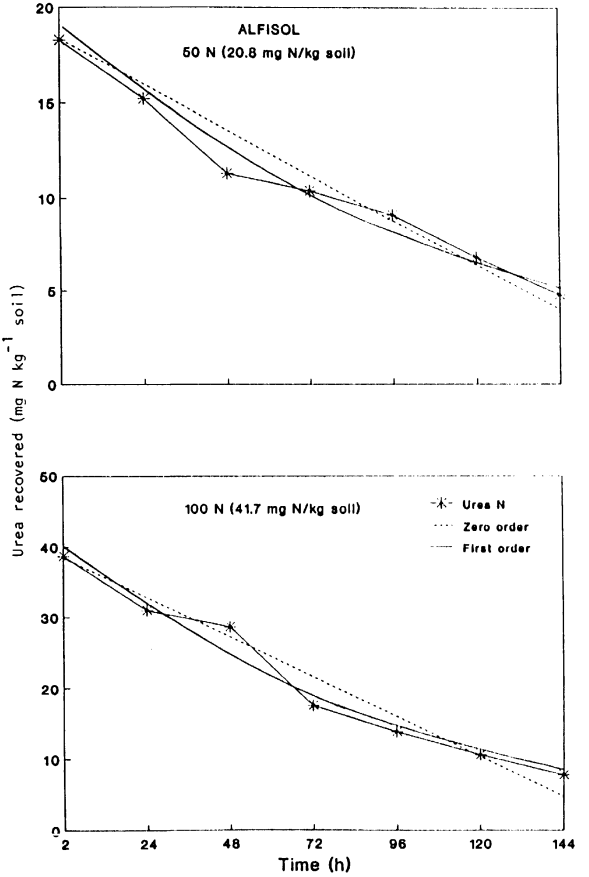


Figure 8: Exp.2: Field disappearance of urea-N from 0-15 cm, after application of 50 and 100 kg N ha^{-1} as urea. The zero and first order relationships are:

50 N : Zero order $Y = 18.5 - 0.1x$ $R^2 = 0.93$

First order $Y = 19.5e^{-0.009t}$ $R^2 = 0.99$

100 N : Zero order $Y = 38.6 - 0.24x$ $R^2 = 0.95$

First order $Y = 41.1e^{-0.01t}$ $R^2 = 0.99$

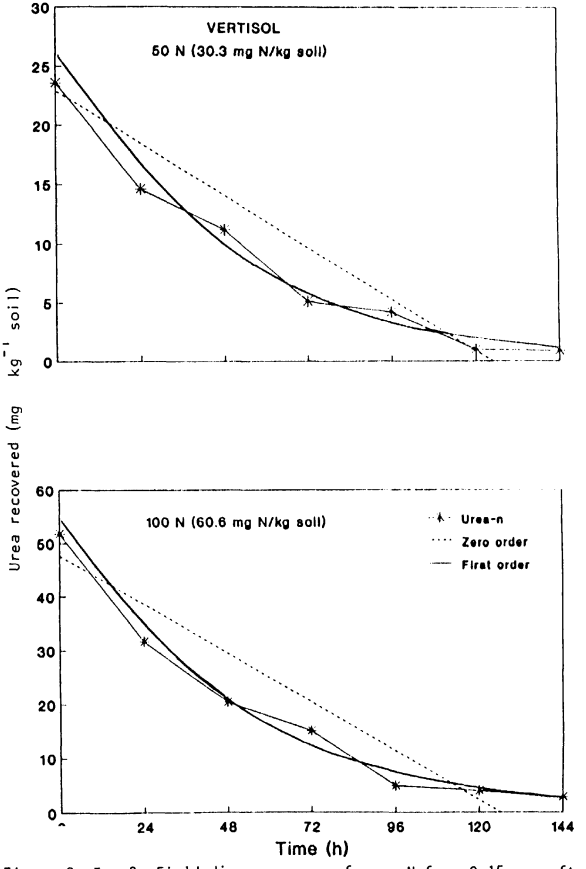


Figure 9: Exp.2: Field disappearance of urea-N from 0-15 cm, after application of 50 and 100 kg N ha^{-1} as urea. The zero and first order relationships are:

50 N	: Zero order	$Y = 23.1 - 0.19x$	$R^2 = 0.83$
	First order	$Y = 27.4e^{-0.021t}$	$R^2 = 0.98$
100 N	: Zero order	$Y = 48.1 - 0.38x$	$R^2 = 0.84$
	First order	$Y = 57.1e^{-0.021t}$	$R^2 = 0.99$

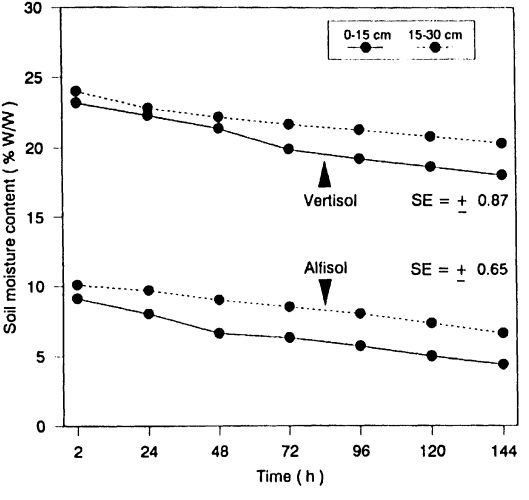


Figure.10 Exp.2: Soil moisture contents in 0-15 and 15-30 cm depths.

Table 11. Experiment 2. Soil temperature (°C) recorded at ICRISAT meterology observatory* during the conduct of Experiment 2, 17-23 December 1986.

Soil depth	Recording time (h)	Date							Mean
		17	18	19	20	21	22	23	
0-15 cm	0717	25.7	25.0	25.0	25.0	24.5	24.5	24.2	24.8
	1417	27.8	26.8	27.0	28.0	26.5	27.6	27.5	27.5

* Vertisol

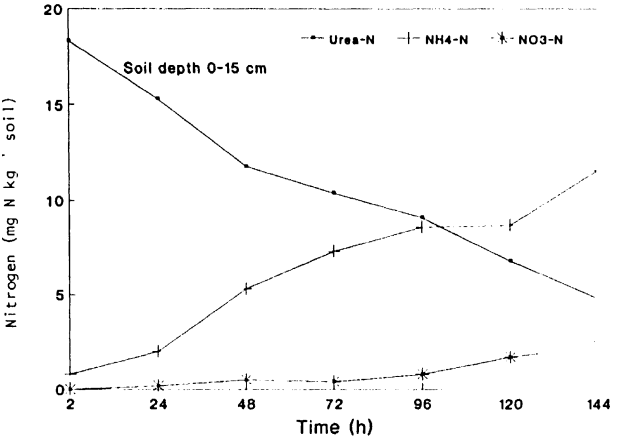


Figure 11: Exp.2: Urea derived inorganic nitrogen in the Alfisol after application of 50 kg urea-N ha^{-1}.

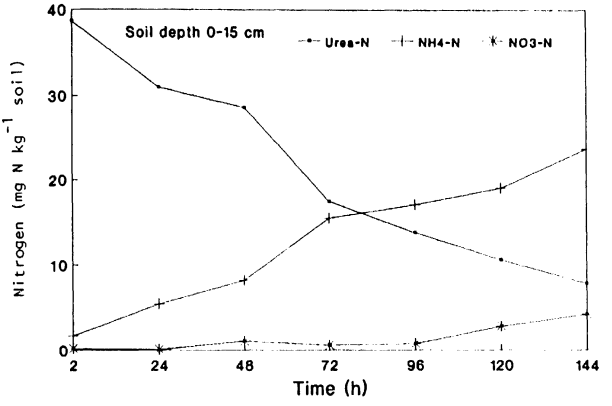


Figure 12: Exp. 12: Urea derived inorganic nitrogen in the Alfisol after application of 100 kg N ha^{-1}.

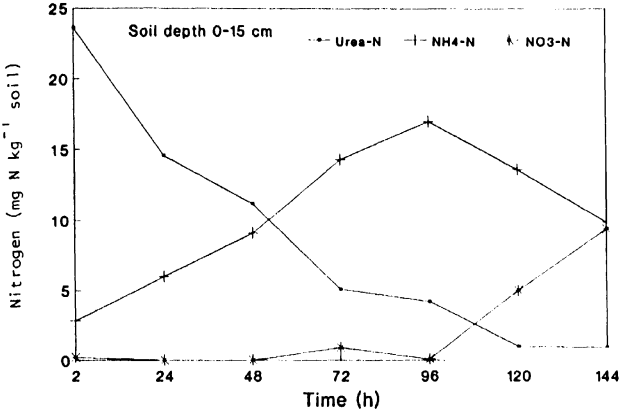


Figure 13: Exp.2: Urea derived inorganic nitrogen in the Vertisol after application of 50 kg N ha^{-1}.

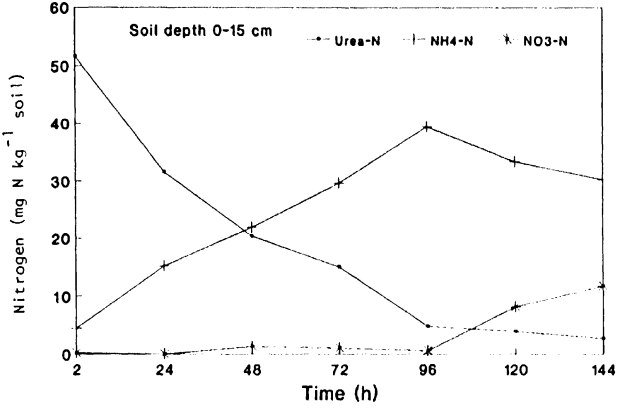


Figure 14: Exp.2: Urea derived inorganic nitrogen in the Vertisol after application of 100 kg N ha^{-1}.

4.1.3 Field Experiment 3. Microplots - Urea Added in Solution is Mixed with Moist Soil

4.1.3.1 Urea Hydrolysis

In this experiment, urea solution was mixed with the soil in small microplots for destructive sampling. Not all the urea applied was recovered at the zero time sampling. In The Alfisol, 97 per cent of applied urea was recovered in the 50 and 100 N treatments and in the Vertisol the urea recovery was 92 per cent in the 50N treatment and 95 per cent in the 100 N treatment. Most of the applied urea (>95 per cent) recovered at zero time sampling in both soils was hydrolysed within 24 hours of urea application, and not more than 1 mg urea-N kg^{-1} soil moved beyond the 5-cm depth (Tables 13 and 14). No urea remained in the Alfisol after 72 hours or in the Vertisol after 120 hours.

4.1.3.2 Kinetics of Urea Hydrolysis

Urea hydrolysis appeared to follow first order reaction kinetics in both the Alfisol (Figure 15) and Vertisol (Figure 16) although the lack of measurements covering the period between 0 and 95 per cent hydrolysis of urea indicates the need for more frequent measurement.

The first order reaction rates for urea-N hydrolysis in the Alfisol were 13 and 15 per cent per hour in the 50 and 100 N treatments (Figure 15). In the Vertisol, the first order reaction rates for urea-N hydrolysis were 14 and 16 per cent per hour in the 50 and 100 N treatments. Urea-N

hydrolysis rates in the two soils appeared to be similar, though urea remained in the soil in the Vertisol for a longer period than in the Alfisol.

4.1.3.3 Effects of Environmental Factors

Changes in soil moisture content in the Alfisol and the Vertisol are shown in Figure 17. In the Alfisol at the 0-5 cm depth, soil moisture in microplots decreased by 6 per cent within 72 hours. During this time, all the urea present in the soil was hydrolysed. Maximum urea hydrolysis occurred while the soil moisture was changing from 15 per cent to 11 per cent at the 0-5 cm depth in the first 24 hours after urea application. In the Vertisol, soil moisture content decreased from 36 per cent to 30 per cent in the 0-5 cm depth during 120 hours. Maximum urea hydrolysis occurred while soil moisture content decreased from 36 per cent to 33 per cent in the 0-5 cm depth in 24 hours after urea application.

Soil temperatures recorded at the 5 and 10 cm depths in the microplots show that in the Alfisol, the average minimum and maximum temperatures measured at 0930 and 1430 hours were 29 and 35.7^{o}C, at the 5 cm depth (Table 15). In the Vertisol the average minimum and maximum temperatures were 31.7 and 36.4^{o}C at the 5 cm depth at 1030 and 1530 hours (Table 15). Temperatures of the 10 cm depth were 2-3 ^{o}C lower than that at the 5 cm depth. The mean minimum and maximum air temperatures were 16.9 and 29.9^{o}C during the the experiment (Appendix M).

In the Alfisol, urea application caused a very large increase in soil pH, from 5.3 to 6.5 (50 N) and 8.1 (100 N) in the 0-5 cm depth over the first 24 hours after urea application, when most of the urea was hydrolysed (Table 16). In the 50 N treated plots the soil regained its normal pH after 120 hours, but in the 100 N treatment, the soil pH remained higher than that of the 0 N treated plots even after 168 hours. There was little consistent change in soil pH at the 5-10 cm depth. In the Vertisol, urea application and urea hydrolysis did not cause any change in soil pH in either of the two depths sampled.

4.1.3.4 Urea Hydrolysis Products

In the Alfisol and Vertisol, NH_4^+-N rapidly reached a maximum after 24 hours in the 0-5 cm depth, both in the 50 and 100 N treatments (Figures 18-21). This coincided with the hydrolysis of most (> 95 per cent) of the urea applied. Ammonium-N decreased rather slowly so that its concentration at 168 hours was less than 50 per cent of that at 24 hours. In the 5-10 cm depth of the Alfisol, a small but quite distinct NH_4^+-N increase (3-12 mg N kg^{-1} soil) was observed, but this occurred only at about 48 hours for the 100 N and at 72 hours for the 50 N treatments (Figures 18 and 19). Nitrate-N increased rather slowly, commencing only after 72 hours. The changes in NO_2^- -N were not greater than 0.07 mg N kg^{-1} soil.

In the 5-10 cm depth of the Vertisol, small increases in the NH_4^+-N was observed, with maximum increase occurring at about 48 hours after urea application (Figures 20 and 21). These figures also show a distinct increase in NO_2^--N (1-10 mg N kg^{-1} soil) in the 0-5 cm and 5-10 cm depth in the two treatments the 50 and 100 N. The increase in NO_2^--N reached a peak at 72 hours after urea application in the two depths. In the 50 and 100 N treatments NO_3^--N increased only after 72 hours in both two depths, but it continued up to the end of the experimental period. The increase in NO_3^--N nitrogen was accompanied by the decrease in NH_4^+-N and NO_2^--N nitrogen concentrations.

In the Alfisol with 50 kg N ha^{-1} applied, 82 per cent of urea-N hydrolysed was recovered as inorganic-N (Appendix I). In the inorganic nitrogen NH_4^+-N was 59 per cent and the rest was NO_3^--N. In the 100 N treatment (Appendix J) 86 per cent of hydrolysed urea-N was recovered in the inorganic form with 73 per cent of it as NH_4^+-N and 23 per cent as NO_3^--N.

In the Vertisol, the recovery of hydrolysed inorganic nitrogen from hydrolysed urea-N was 88 per cent in the 50 N treatment (Appendix K), with NH_4^+-N NO_2^--N and NO_3^--N contributing 59, 7 and 34 per cent respectively. In the 100 N treatment (Appendix L), the recovery of hydrolysed urea-N in the inorganic form was 90 per cent, and 64 per cent of it was as NH_4^+-N,4 per cent as NO_2^--N and 32 per cent as NO_3^--N nitrogen.

Table 12: Characteristics of the experimental soils

	Alfisol*		Vertisol*	
Depth(cm)	0-5	5-10	0-5	5-10
Organic carbon %	0.26	0.25	0.39	0.36
Total nitrogen %	0.05	0.04	0.06	0.06
Ammonium-N (mg kg^{-1} soil)	10.0	8.7	16.7	16.3
Nitrate-N (mg kg^{-1} soil)	8.8	8.9	11.2	11.5
pH (1:2 H_2O)	5.3	5.5	8.2	8.3
Sand fraction %	84.7	81.0	24.0	25.0
Silt %	4.2	5.0	26.0	24.0
Clay %	11.1	12.0	50.0	51.0
CEC C mole kg^{-1} soil	5.8	6.1	28.0	30.0
Bulk density g/cc	1.50	1.54	1.03	1.03

* Location in ICRISAT : Alfisol : Field RW 3
Vertisol: Field BW 6

Table 13. Experiment 3: Transformations of urea nitrogen in an Alfisol in the field: urea, ammonium, nitrite and nitrate-N concentrations (mg N Kg^{-1} soil) in unamended and amended soil[a]

Forms of nitrogen	Soil depth cm	Urea-N added kg/ha^{-1}	Time (h) 0	24	48	72	96	120	144	168	SE
Urea-N	0-5	100	128.6	3.2	0.4	0	0	0	0	0	
		50	63.8	2.6	0.9	0	0	0	0	0	
		0	0	0	0	0	0	0	0	0	
											±0.53
	5-10	100	0	1.0	0.6	0	0	0	0	0	
		50	1.0	0.7	0	0	0	0	0	0	
		0	0	0	0	0	0	0	0	0	
NH_4^+-N	0-5	100	1.6	110.4	109.4	102.2	95.2	90.0	74.5	73.0	
		50	1.2	53.9	52.7	53.1	46.0	40.4	32.1	28.0	
		0	1.3	1.3	1.4	1.3	0.8	0.8	0.6	0.8	
											±1.8
	5-10	100	1.3	13.9	14.9	13.1	12.2	11.4	10.8	9.4	
		50	1.1	4.1	5.7	6.5	5.4	5.7	4.8	5.1	
		0	1.4	1.3	1.0	1.0	1.1	1.1	0.9	1.2	
NO_2^--N	0-5	100	0.01	0.01	0.05	0.04	0.07	0.01	0	0	
		50	0.01	0.01	0.02	0.02	0.02	0.01	0	0	
		0	0.02	0	0.02	0.01	0	0	0	0	
											±0.07
	5-10	100	0.01	0.01	0.02	0.01	0	0	0	0	
		50	0.01	0.01	0.01	0.02	0	0	0	0	
		0	0.03	0	0.01	0.01	0	0	0	0	
NO_3^--N	0-5	100	2.3	2.3	2.5	2.8	7.0	10.3	22.1	24.7	
		50	2.4	2.8	2.8	3.9	5.3	10.9	13.9	17.7	
		0	2.0	2.4	2.1	2.9	2.0	3.0	2.0	2.0	
											±0.95
	5-10	100	1.4	2.1	1.9	2.6	3.9	7.2	9.3	9.9	
		50	1.8	2.4	2.0	2.8	2.9	4.6	7.8	8.9	
		0	1.4	1.3	1.4	2.5	1.6	2.3	2.7	2.7	

[a] Urea solution was mixed with the soil from 0-5 cm depth

Table 14. Experiment 3: Transformations of urea nitrogen in a Vertisol in the field: urea, ammonium, nitrite and nitrate-N concentrations (mg N kg^{-1} soil) in unamended and amended soil[a]

Forms of nitrogen	Soil depth cm	Urea-N added kg/ha-1	Time (h) 0	24	48	72	96	120	144	168	SE
Urea-N	0-5	100	183.7	4.1	3.0	1.8	1.4	0.2	0	0	
		50	89.7	3.0	1.7	1.1	0.6	0	0	0	
		0	0	0	0	0	0	0	0	0	
											±1.4
	5-10	100	0	0	0.4	0.2	0	0	0	0	
		50	0	0	0.3	0.1	0	0	0	0	
		0	0	0	0	0	0	0	0	0	
NH_4^+-N	0-5	100	3.5	167.0	157.0	156.8	138.4	122.8	115.7	103.0	
		50	2.6	78.4	73.9	70.9	62.1	56.3	50.2	45.6	
		0	2.5	2.7	2.9	3.1	2.1	2.6	3.0	1.3	
											±0.61
	5-10	100	2.3	9.2	9.2	9.4	8.5	8.4	6.5	5.4	
		50	2.4	8.5	7.6	8.4	6.4	7.1	5.7	4.4	
		0	2.2	2.3	1.9	3.9	2.1	3.7	2.7	1.9	
NO_2^--N	0-5	100	0.1	4.0	9.6	10.6	8.4	8.1	6.9	4.1	
		50	0.1	2.8	6.3	8.7	7.3	5.5	4.7	3.8	
		0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
											±2.0
	5-10	100	0.1	1.7	6.3	6.4	4.4	2.7	2.2	1.9	
		50	0.1	1.5	2.8	3.6	2.8	2.1	1.8	1.7	
		0	0.04	0	0.1	0.2	0.2	0.1	0.2	0.1	
NO_3^--N	0-5	100	9.4	11.4	11.3	11.5	26.3	37.2	46.5	60.2	
		50	13.5	10.4	10.9	11.0	21.9	28.0	34.6	37.6	
		0	12.6	10.6	11.7	12.8	15.5	15.0	17.1	17.4	
											±5.0
	5-10	100	9.6	10.8	12.4	13.3	18.9	21.4	21.8	24.2	
		50	9.2	10.4	12.8	13.8	17.6	19.9	19.4	20.3	
		0	9.7	10.7	13.4	13.4	14.2	14.5	13.4	13.4	

[a] Urea solution was mixed with the soil from 0-5 cm depth

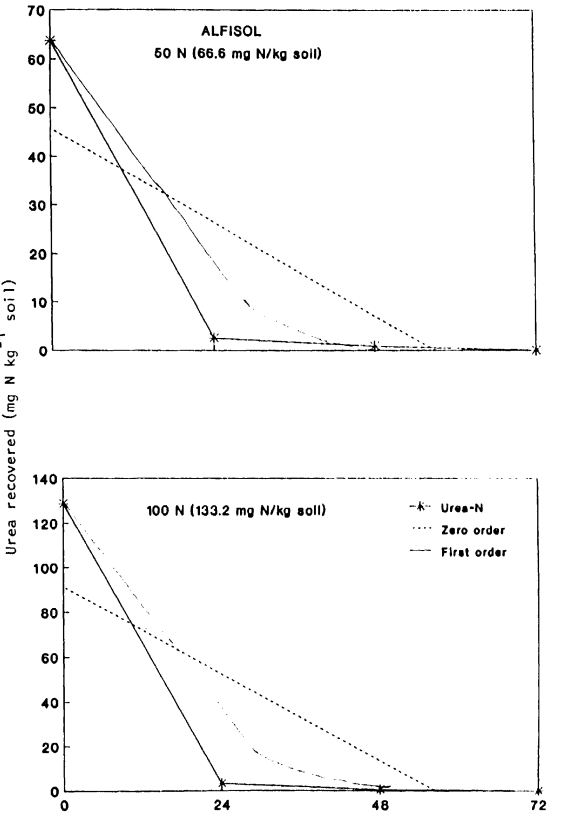
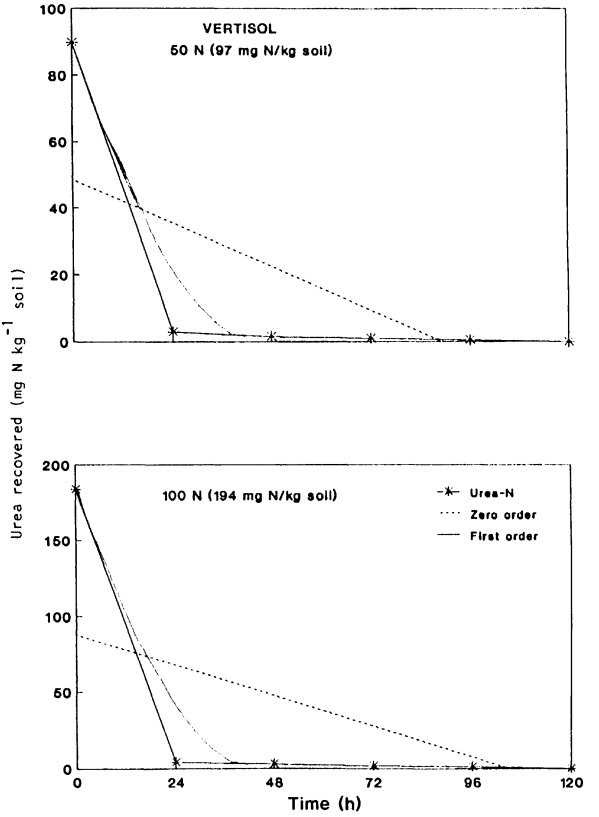


Figure 15: Exp.3: Field disappearance of urea-N from 0-5 cm, after application of 50 and 100 kg N ha^{-1} as urea. The zero and first order relationships are:

50 N	:	Zero order	$Y = 45.81 - 0.80x$	$R^2 = 0.45$
		First order	$Y = 63.8e^{-0.13t}$	$R^2 = 0.99$
100 N	:	Zero order	$Y = 91.4 - 1.62x$	$R^2 = 0.43$
		First order	$Y = 128.6e^{-0.15t}$	$R^2 = 0.99$



Figxre 16: Exp.3: Field disappearance of urea-N from 0-5 cm, after application of 50 and 100 kg N ha^{-1} as urea. The zero and first order relationships are:

50 N	:	Zero order	$Y = 48.6 - 0.54x$	$R^2 = 0.32$
		First order	$Y = 89.8e^{-0.14t}$	$R^2 = 0.99$
100 N	:	Zero order	$Y = 87.8 - 0.83x$	$R^2 = 0.27$
		First order	$Y = 183.7e^{-0.16t}$	$R^2 = 0.99$

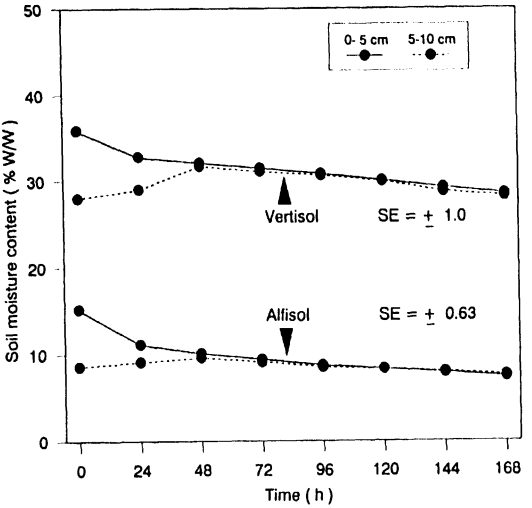


Figure.17 Exp.3: Soil moisture contents in 0-5 and 5-10 cm depths.

Table 15. Experiment 3: Soil temperatures (°C) in microplots at the Alfisol and Vertisol field sites the conduct of experiment, 23-31 October 1987

Soil depth cm	Recording time	Dates 23	24	25	26	27	28	29	30	31	Mean
					Alfisol						
5	0930	28.0	28.0	28.5	29.0	29.2	30.0	30.0	30.4		29.1
	1430	34.0	34.5	35.0	35.2	36.0	36.3	37.0	37.5		35.7
10	0930	26.8	27.0	27.4	28.0	28.0	28.5	29.0	29.2		28.0
	1430	31.3	31.8	32.3	32.5	33.0	33.0	34.0	34.2		32.8
					Vertisol						
5	1030		30.0	30.0	30.0	33.0	34.0	32.5	32.0	32.0	31.7
	1530		35.6	36.0	36.2	37.0	37.0	36.0	36.3	37.0	36.4
10	1030		28.5	29.0	29.2	30.0	31.0	30.0	29.5	30.0	29.7
	1530		34.0	33.5	34.0	35.0	35.0	33.0	33.0	35.0	34.1

Table 16. Experiment 3: Soil pH values measured after urea application

Soil	Soil depth cm	Urea-N added kg/ha^{-1}	Time (h)							
			0	24	48	72	96	120	144	168
Alfisol	0-5	100		8.1	7.9	7.8	7.6	7.5	6.3	6.1
		50		6.5	6.3	6.4	6.8	6.3	5.4	5.4
		0	5.3	5.1	5.4	5.5	5.4	5.7	5.4	5.5
	5-10	100		5.7	4.8	5.0	5.1	5.0	5.1	5.0
		50		6.0	4.7	5.0	4.9	5.0	5.0	4.9
		0	5.3	6.0	5.0	5.6	5.1	4.8	5.3	4.8
Vertisol	0-5	100		8.2	8.4	8.3	8.3	7.8	7.8	7.7
		50		8.1	8.2	8.3	8.4	8.3	8.3	8.2
		0	8.2	8.2	8.1	8.0	8.3	8.3	8.3	8.2
	5-10	100		8.4	8.2	7.9	8.2	7.8	8.1	8.2
		50		8.2	8.1	8.2	8.1	8.3	8.0	8.0
		0	8.3	8.3	8.1	8.2	8.3	8.4	8.5	8.3

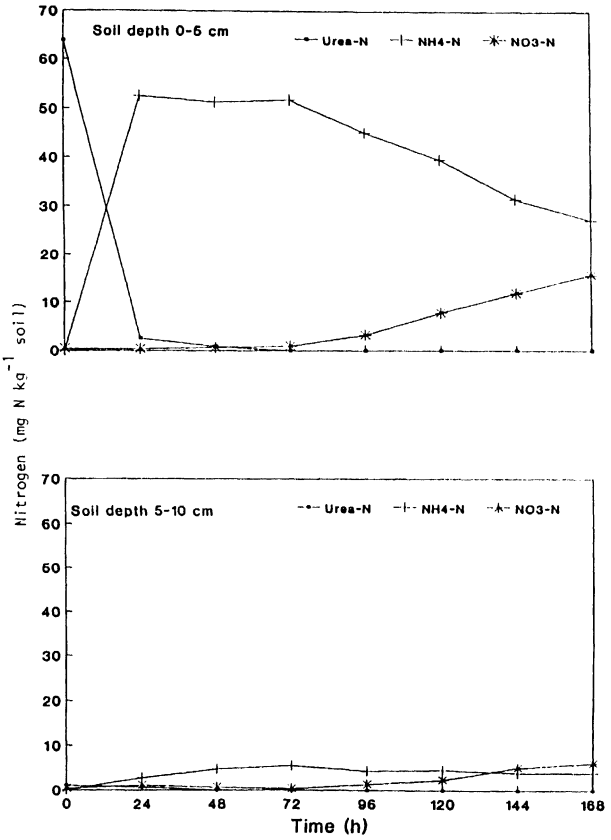


Figure 18: Exp.3: Urea derived inorganic nitrogen in the Alfisol after application of 50 kg N ha^{-1}.

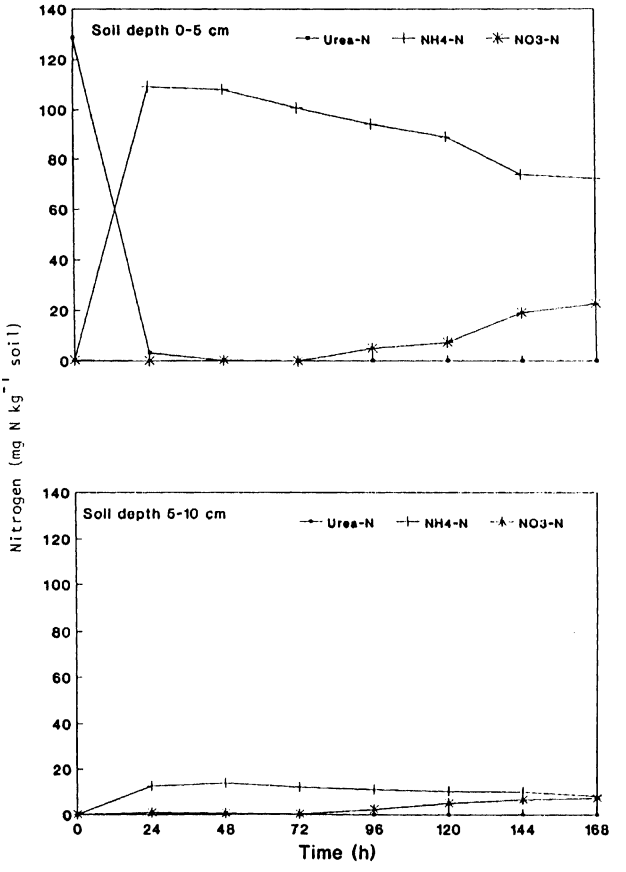


Figure 19: Exp.3: Urea derived inorganic nitrogen in the Alfisol after application of 100 kg N ha^{-1}.

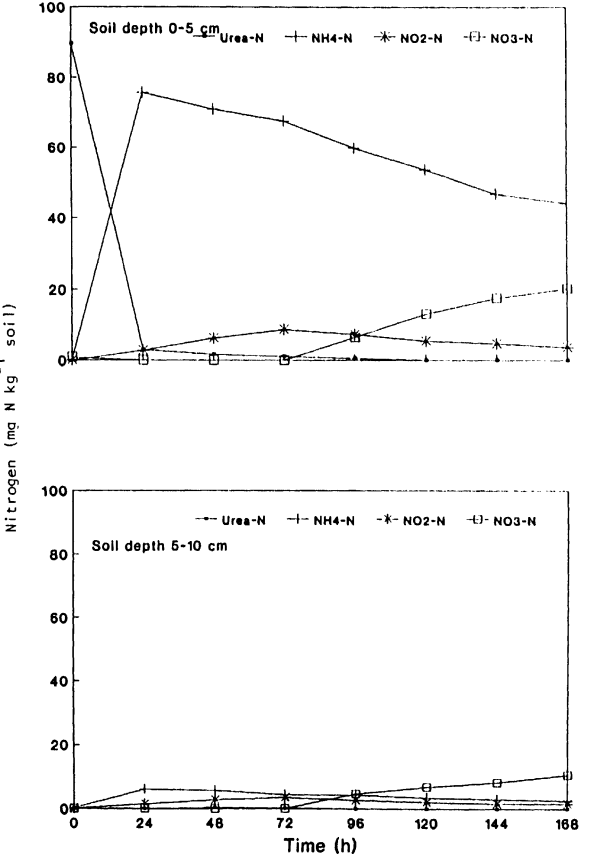


Figure 20: Exp.3: Urea derived inorganic nitrogen in the Vertisol after application of 50 kg N ha^{-1}.

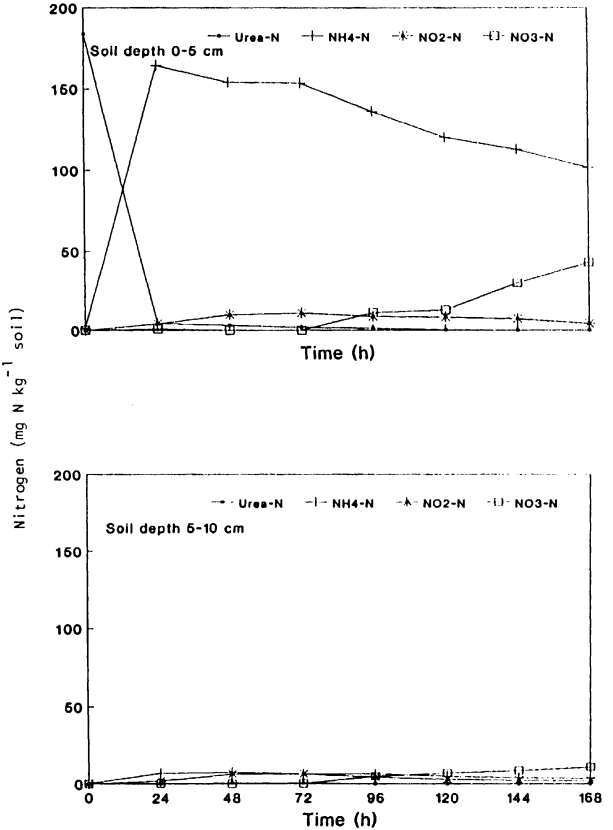


Figure 21: Exp.3: Urea derived inorganic nitrogen in the Vertisol after application of 100 kg N ha^{-1}.

4.1.4 Field Experiment 4. Microplots Frequent Measurements after Urea in Solution Mixed with Moist Soils in Microplots

4.1.4.1 Urea hydrolysis

In this experiment also not all the urea applied could be recovered at "zero time". For the Alfisol only 62.8 and 128.6 mg urea-N kg^{-1} soil was recovered from the 66.6 and 133.2 mg urea-N kg^{-1} soil originally applied, giving a recovery of 94 and 97 per cent. For the Vertisol, the "zero time" recoveries were 89.9 and 182.6 mg urea-N kg^{-1} soil from the 97 and 194 mg urea-N kg^{-1} soil, giving recoveries of 93 and 94 per cent.

As in the previous, experiment most of the applied urea (>95 per cent) recovered in zero hour samples was hydrolysed within 24 hours in both the Alfisol (Table 17) and the Vertisol (Table 18). In the Vertisol urea did not move beyond the 5 cm depth and in the Alfisol only a small proportion (< 2 mg N kg^{-1} soil) of urea was recovered in the 5-10 cm depth after 24 hours.

4.1.4.2 Kinetics of Urea Hydrolysis

In both the Alfisol (Figure 22) and the Vertisol (Figure 23) urea hydrolysis fitted closely to the first order reaction kinetics for both the 50 and 100 N treatments (R^2 > 0.97) rather than zero order (R^2 < 0.32). For 100 N treatment in the two soils, the data give the impression that the fit to a first order reaction would be even better if

only results from the 4 hours onwards are considered, that is if there was a lag phase of 2-3 hours before hydrolysis proceeded effectively.

The first order reaction rates of urea-N hydrolysis in the Alfisol were 13 and 12 per cent per hour in the 50 and 100 N treatments. In the Vertisol, the urea-N hydrolysis rates were 15 and 13 per cent per hour for the 50 and 100 N treatments. Thus urea-N hydrolysis rates were higher in the Vertisol than in the Alfisol, for both nitrogen treatments.

4.1.4.3 Effects of Environmental Factors

The decrease in soil moisture content at 24 hours was 8 per cent in the two depths, 0-5 and 5-10 cm in the Alfisol. In the Vertisol, the moisture content decreased by 7 per cent in the 0-5 cm depth, and by 6 per cent in the 5-10 cm depth during the 24 hour period (Figure 24). The decrease was relatively rapid in the Alfisol over the first four hours, indicating a rapid percolation of water held in excess of field capacity, but the decrease was quite slow after 8 hours. In the Vertisol, the decline in moisture content was fairly constant throughout the experimental period.

In the Alfisol, over half of the urea hydrolysis occurred while moisture content of the 0-5 cm depth was rapidly changing from 20 per cent to 14 per cent in the first 8 hours after urea application. In the Vertisol over 60 per cent of urea was hydrolysed in the first 8 hours after the urea application when moisture content declined slowly from 47 per

cent to 46 per cent. The moisture contents were considerably higher than those in the earlier experiments.

Soil temperatures, recorded at the 5 and 10 cm depths in microplots (Table 19) show that at the 5 cm depth a temperature above 32°C prevailed in the Alfisol and above 38°C in the Vertisol, between 0-12 hours when maximum urea hydrolysis occurred. These temperatures were several degrees (3-6 °C) higher than in the previous experiment.

The average minimum and maximum air temperatures were 21.8°C and 35.6°C during the experimental period in the Alfisol and they were 19.4°C and 36.2°C during the study in the Vertisol. (Appendix R).

4.1.4.4 Urea hydrolysis products

In the Alfisol and Vertisol, NH_4^+-N was the only form of inorganic nitrogen that accumulated substantially during the short 24 hours period. Figures 25-28 show NH_4^+ -N concentration in the 0-5 and 5-10 cm soil depths following urea hydrolysis in the 50 and 100 N treated plots of the Alfisol and Vertisol.

In the 50 N treatment in the Alfisol 95 per cent of the applied urea was hydrolysed within 24 hours and 98 per cent of this hydrolysed urea-N was recovered as NH_4^+-N (Appendix N). Similarly in the 100 N treatment 96 per cent of the applied urea was hydrolysed in 24 hours and 99 per cent of this hydrolysed urea-N was recovered as NH_4^+-N (Appendix O).

In the Vertisol, more than 98 per cent of the applied urea was hydrolysed within 24 hours in the 50 and 100 N treatments and over 97 per cent of this hydrolysed urea was recovered as NH_4^+-N (Appendices P and Q).

Table 17. Experiment 4: Transformations of urea nitrogen in an Alfisol in the field: urea, ammonium nitrate and nitrate-N concentrations (mg N kg^{-1} soil) in unamended and amended soil[a]

Forms of nitrogen	Soil depth cm	Urea-N added kg/ha^{-1}	Time (h) 0	4	8	12	16	20	24	SE
Urea-N	0-5	100	128.6	105.8	59.7	25.5	13.6	6.7	3.5	
		50	62.8	44.0	29.5	9.1	5.5	3.6	1.9	
		0	0	0	0	0	0	0	0	
										±1.4
	5-10	100	0	6.0	3.9	3.2	2.8	2.4	1.7	
		50	0	4.1	2.6	2.2	2.0	1.7	1.2	
		0	0	0	2.2	0	2.0	0	0	
NH_4^+-N	0-5	100	1.5	16.4	62.3	95.8	107.9	112.8	116.6	
		50	1.5	14.7	30.3	48.3	51.8	54.7	56.2	
		0	1.9	1.9	1.8	1.7	1.7	1.7	1.5	
										±0.99
	5-10	100	1.4	2.2	2.8	3.3	4.1	4.7	5.4	
		50	1.4	2.1	2.3	3.1	3.2	2.3	3.7	
		0	1.4	1.9	1.4	1.4	1.5	1.4	1.5	
NO2-2	0-5	100	0.01	0.01	0.02	0.03	0.02	0.02	0.02	
		50	0.01	0.01	0.01	0.02	0.02	0.01	0.01	
		0	0.02	0.01	0.01	0.01	0.01	0.01	0.02	
										±0.01
	5-10	100	0	0	0	0	0	0	0.01	
		50	0	0	0	0.01	0	0.01	0.01	
		0	0.01	0	0	0.01	0.01	0.01	0	
NO_3^--N	0-5	100	2.3	2.6	2.6	2.5	2.5	2.5	2.8	
		50	2.5	2.5	2.4	2.5	2.6	2.8	3.0	
		0	2.5	2.6	2.7	2.8	2.9	1.8	2.0	
										±0.42
	5-10	100	1.8	1.8	1.6	1.7	1.7	1.8	2.0	
		50	1.7	1.6	1.6	1.8	1.7	1.8	1.9	
		0	1.8	1.8	2.1	2.0	2.0	1.7	1.9	

[a] Urea solution was mixed with the soil from 0-5 cm depth

Table 18. Experiment 4: Transformations of urea nitrogen in a Vertisol in the field: urea, ammonium, nitrite and nitrate-N concentrations (mg N kg^{-1} soil) in unamended and amended soil[a]

Forms of nitrogen	Soil depth cm	Urea-N added kg/ha^{-1}	Time (h) 0	4	8	12	16	20	24	SE
Urea-N	0-5	100	182.6	134.9	55.4	34.0	23.7	10.3	2.0	
		50	89.9	45.6	33.1	11.4	7.9	5.4	1.4	
		0	0	0	0	0	0	0	0	
										±1.7
	5-10	100	0	0	0	0	0	0	0.7	
		50	0	0	0	0	0	0	0	
		0	0	0	0	0	0	0	0	
NH_4^+-N	0-5	100	2.8	46.4	124.7	143.6	154.4	165.6	178.8	
		50	3.0	43.4	54.4	70.2	78.0	83.3	88.7	
		0	3.2	2.8	2.4	2.4	2.7	2.4	3.4	
										±0.84
	5-10	100	2.0	2.7	3.8	3.5	2.3	3.7	3.3	
		50	2.0	2.3	2.2	2.3	3.3	3.5	2.7	
		0	1.9	1.5	2.1	2.4	2.4	2.5	3.0	
NO2-2	0-5	100	0.09	0.22	0.35	0.43	1.60	1.48	0.79	
		50	0.07	0.19	0.24	0.31	0.89	0.82	0.32	
		0	0.06	0.05	0.08	0.06	0.05	0.07	0.10	
										±0.02
	5-10	100	0.07	0.09	0.09	0.13	0.15	0.13	0.16	
		50	0.09	0.06	0.07	0.11	0.10	0.09	0.07	
		0	0.08	0.05	0.06	0.07	0.07	0.06	0.06	
NO_3^--N	0-5	100	9.0	8.6	9.2	10.1	9.7	10.3	13.0	
		50	9.7	9.0	9.1	9.0	8.8	9.3	10.3	
		0	10.9	9.9	10.4	10.4	9.4	9.4	10.0	
										±0.77
	5-10	100	7.0	6.8	7.3	7.4	7.0	7.1	7.7	
		50	7.3	8.1	7.9	7.5	7.3	8.7	7.3	
		0	6.5	7.1	7.0	7.4	8.1	7.9	7.4	

[a] Urea solution was mixed with the soil from 0-5 cm depth

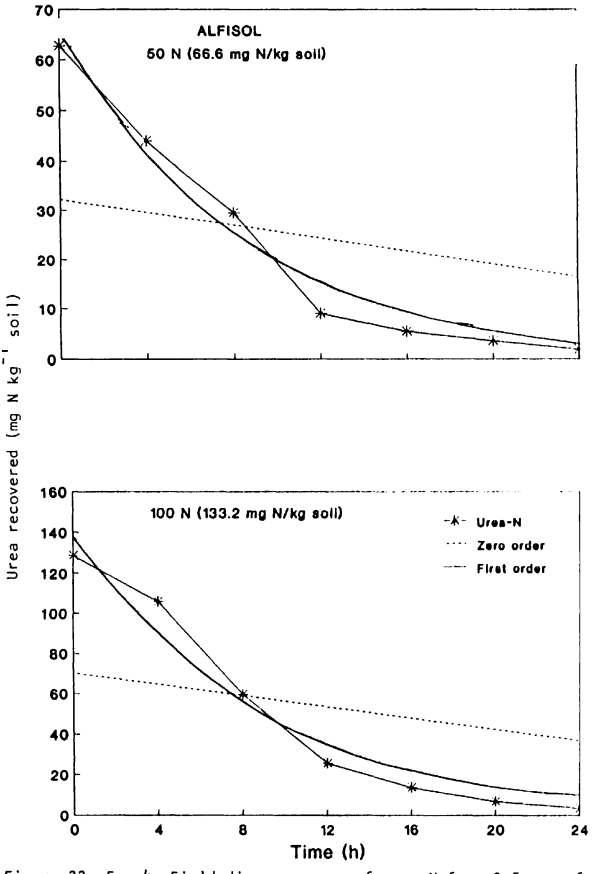


Figure 22: Exp.4: Field disappearance of urea-N from 0-5 cm, after application of 50 and 100 kg N ha^{-1} as urea. The zero and first order relationships are:

50 N	: Zero order	$Y = 32.1 - 0.65x$	$R^2 = 0.29$
	First order	$Y = 65.5e^{-0.13t}$	$R^2 = 0.98$
100 N	: Zero order	$Y = 70.3 - 1.4x$	$R^2 = 0.31$
	First order	$Y = 138.4e^{-0.12t}$	$R^2 = 0.97$

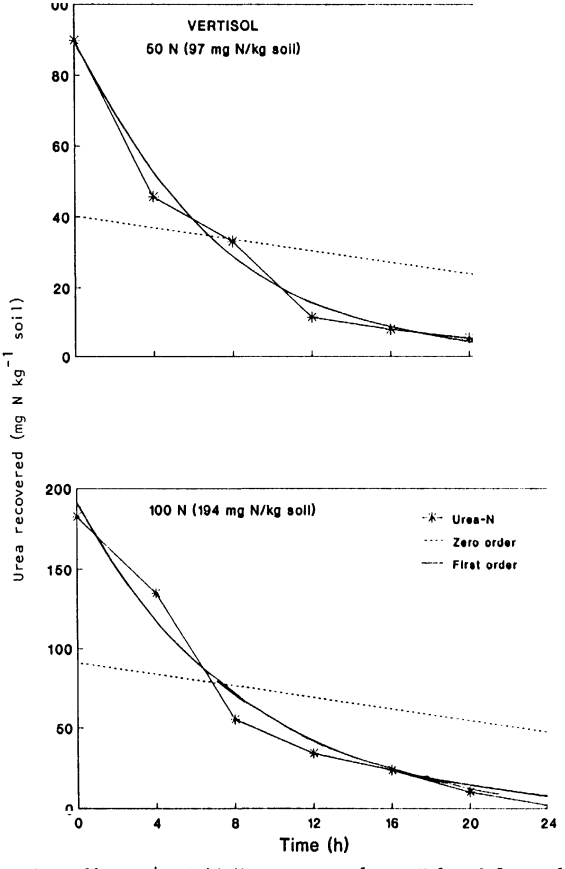


Figure 23: Exp.4: Field disappearance of urea-N from 0-5 cm, after application of 50 and 100 kg N ha^{-1} as urea. The zero and first order relationships are:

50 N	Zero order	$Y = 40.2 - 0.81x$	$R^2 = 0.24$
	First order	$Y = 89.2e^{-0.15t}$	$R^2 = 0.99$
100 N	Zero order	$Y = 91.0 - 1.82x$	$R^2 = 0.27$
	First order	$Y = 190.6e^{-0.13t}$	$R^2 - 0.98$

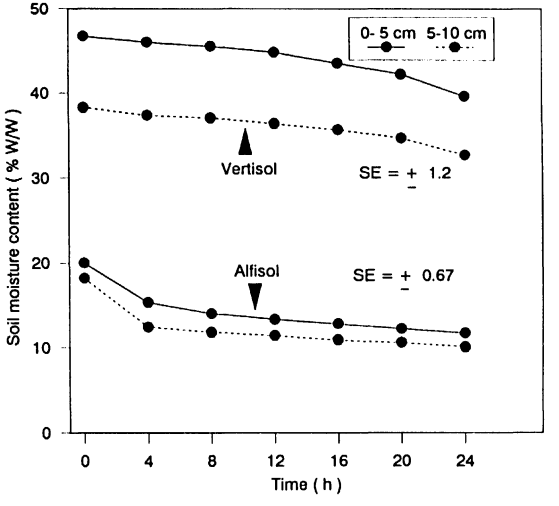


Figure.24 Exp.4: Soil moisture contents in 0-5 and 5-10 cm depths.

Table 19. Experiment 4: Soil temperatures (°C) in microplots at the Alfisol and Vertisol field sites during the conduct of experiment

Date	Soil	Soil depth	Time of day (h)							Mean
1988		cm	12	16	20	0	04	08	12	
February										
27-28	Alfisol	5	35.2	38.0	32.6	28.0	24.0	28.5	35.0	31.6
		10	33.5	36.0	32.5	24.2	19.5	26.0	33.5	29.3
March										
19-20	Vertisol	5	38.0	41.0	38.0	28.5	24.5	30.0	41.5	34.5
		10	36.0	38.0	35.0	26.0	20.0	28.5	37.0	31.5

Table 20. Experiment 4: Soil pH values, measured after urea application

Soil	Soil depth cm	Urea-N added kg/ha^{-1}	Time (h) after urea application						
			0	4	8	12	16	20	24
Alfisol	0-5	100		8.3	8.4	8.2	8.6	8.9	9.2
		50		8.3	8.7	8.3	8.2	8.0	8.1
		0	5.3	6.2	6.4	5.8	5.4	5.4	5.3
	5-10	100		6.1	6.1	6.0	5.9	6.6	5.8
		50		5.2	6.4	6.2	6.4	6.3	6.1
		0	5.2	5.6	5.4	5.2	5.7	5.9	5.4
Vertisol	0-5	100		8.2	8.3	8.4	8.2	8.3	8.4
		50		8.4	8.4	8.5	8.1	8.3	8.5
		0	8.4	8.5	8.2	8.4	8.3	8.3	8.5
	5-10	100		7.9	8.0	8.1	7.9	8.1	8.0
		50		8.2	8.2	8.1	7.9	8.1	8.1
		0	8.1	8.3	8.1	8.4	8.1	8.2	8.4

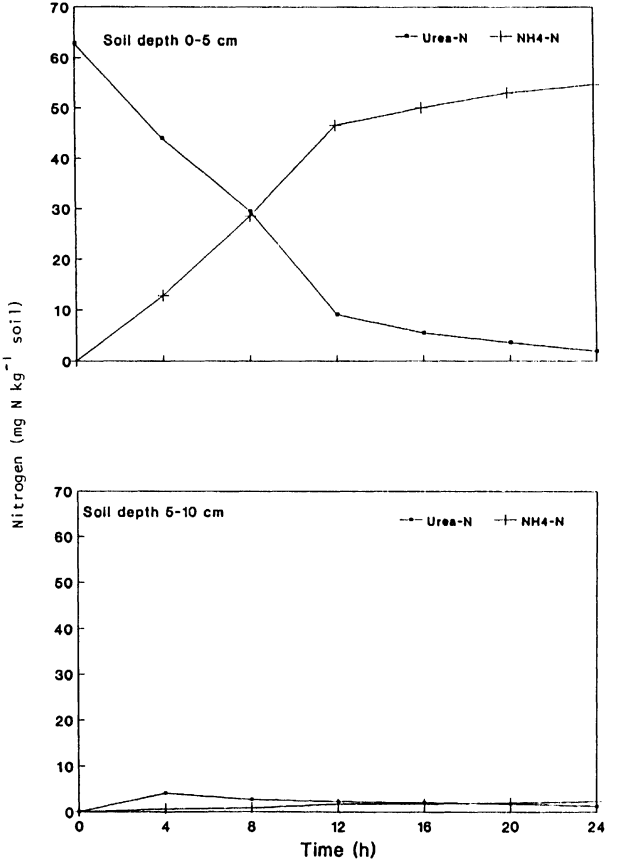


Figure 25: Exp.4: Urea derived inorganic nitrogen in the Alfisol after application of 50 kg N ha^{-1}.

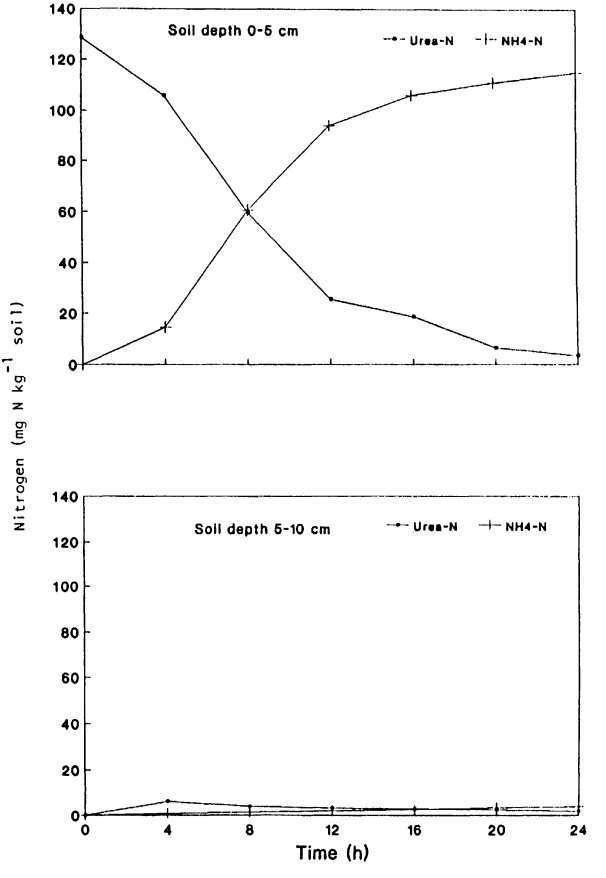


Figure 26: Exp.4: Urea derived inorganic nitrogen in the Alfisol after application of 100 kg N ha^{-1}.

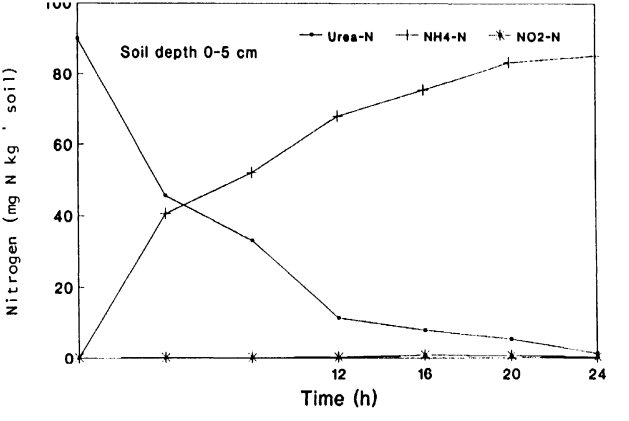


Figure 27: Exp.4: Urea derived inorganic nitrogen in the Vertisol after application of 50 kg N ha^{-1}.

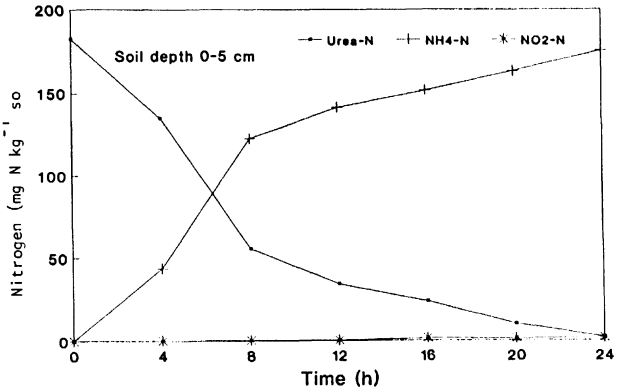


Figure 28: Exp.4: Urea derived inorganic nitrogen in the Vertisol after application of 100 kg N ha^{-1}.

4.1.5 Incubation Experiment - Urea in Solution Mixed with Air Dried Soil Samples 0-5 cm Depth.

4.1.5.1 Urea Hydrolysis

In this experiment also urea hydrolysis was studied at 4 hour intervals upto 24 hours. In the Alfisol, over 98 per cent of the urea-N was recovered at the "zero time" sampling, and in the Vertisol over 99 per cent of urea was recovered. In this laboratory experiment as in the previous field experiment most of the urea (> 97 per cent) recovered in zero hour samples was hydrolysed within 24 hours in both the Alfisol (Table 21), and the Vertisol (Table 22). In the Alfisol within 12 hours over 75 per cent urea-N in zero hour samples was hydrolysed for 50 and 100 N treatments. In the Vertisol, after 12 hours, over 85 per cent of the urea recovered in zero hour samples was hydrolysed in the 50 N treatment, but only 54 per cent of applied urea was hydrolysed in the 100 N treatment.

4.1.5.2 Urea Hydrolysis Kinetics

Figures 29 and 30 show that urea hydrolysis fitted the first order reaction kinetics more closely than the zero order reaction kinetics in the 50 and 100 N treatments in the Alfisol and the 50 N treatment in the Vertisol. However, in the 100 N treatment in the Vertisol (Figure 30), the R^2 values (0.97) were same for the zero order and first order reaction equations.

From the first order reaction relationship, 11 per cent urea N per hour was hydrolysed in the Alfisol in the two treatments (Figure 29). In the Vertisol, 17 per cent urea-N per hour was hydrolysed in the 50 N treatment and 8.8 per cent urea N per hour was hydrolysed in the 100 N treatment. The reason for the low rate in the Vertisol 100 N treatment is not known.

There appears to be a lag phase in urea hydrolysis between 0 and 8 hours for both nitrogen treatments in the Alfisol but not in the Vertisol.

4.1.5.3 Effects of Environmental Factors

In this incubation experiment in the laboratory, environmental factors were kept constant at the imposed levels i.e. a constant temperature of 32°C and moisture contents of 24 per cent (W/W) for the Alfisol and 40 per cent (W/W) for the Vertisol.

4.1.5.4 Urea Hydrolysis Products

In the Alfisol, only NH_4^+-N accumulated following urea hydrolysis (Figures 31 and 32). The accumulated inorganic nitrogen in the Vertisol (Figures 33 and 34) includes NO_2^--N besides NH_4^+-N.

In the Alfisol >95 of urea hydrolysed was recovered as inorganic nitrogen and all of it was NH_4^+-N in the 50 and 100 N treatments (Appendices S and T). In the Vertisol 90 per cent hydrolysed urea was recovered in the 50 N treatment

Table 21. Experiment 5: Transformations of urea nitrogen in soil samples from 0-5 cm depth of an Alfisol; urea, ammonium, nitrite and nitrate-N concentrations (mgN kg^{-1} soil) in unamended and amended soil[a]

Forms of Nitrogen	Urea-N[b] added	Time (h)							SE
		0	4	8	12	16	20	24	
Urea-N	100	131.8	118.7	105.9	21.2	4.4	3.9	2.4	
	50	65.5	55.3	42.8	12.4	2.8	0.9	0.2	
	0	0	0	0	0	0	0	0	±0.99
NH_4^+-N	100	9.9	22.5	33.2	117.3	133.1	134.7	136.1	
	50	9.7	19.4	31.0	60.2	68.6	70.0	72.2	
	0	9.9	9.8	9.7	9.8	9.9	9.7	9.5	±1.1
NO_2^--N	100	0.02	0.02	0.02	0.03	0.03	0.03	0.03	
	50	0.01	0.01	0.02	0.02	0.02	0.02	0.01	
	0	0.02	0.01	0.01	0.01	0.01	0.02	0.01	±0.01
NO_3^--N	100	8.4	8.7	8.6	8.7	9.0	8.9	9.1	
	50	8.5	8.8	9.2	9.4	9.2	8.9	8.5	
	0	8.7	8.7	8.8	8.7	8.9	9.0	8.6	±0.18

[a] Urea solution was added to the soil sample
[b] 66.6 ug urea-N g^{-1} soil was added for 50 kg N ha^{-1}

Table 22. Experiment 5: Transformations of urea nitrogen in soil samples from 0-5 cm depth of a Vertisol; urea, ammonium, nitrite and nitrate-N concentrations (mgN kg^{-1} soil) in unamended and amended soil[a]

Forms of Nitrogen	Urea-N[b] added	Time (h)							SE
		0	4	8	12	16	20	24	
Urea-N	100	193.6	147.5	122.5	88.5	33.8	21.9	4.3	
	50	96.4	53.8	29.2	12.3	0.2	0.1	0.1	
	0	0	0	0	0	0	0	0	±2.6
NH_4^+-N	100	16.3	55.1	80.9	109.5	164.8	175.9	193.3	
	50	15.9	50.1	76.4	90.8	97.2	97.4	98.5	
	0	15.7	15.2	15.7	16.1	15.5	15.6	15.8	±0.49
NO_2^--N	100	0.06	1.62	2.88	3.90	7.0	7.5	6.5	
	50	0.16	1.88	3.0	4.0	4.13	4.5	4.0	
	0	0.10	0.14	0.16	0.21	0.24	0.2	0.22	±0.23
NO_3^--N	100	10.8	12.1	12.2	11.3	13.3	11.9	12.5	
	50	11.1	10.4	11.1	11.5	12.9	11.0	11.9	
	0	11.3	11.6	10.9	10.4	11.0	12.4	11.5	±0.74

[a] Urea solution was added to the soil sample
[b] 97 ug urea-N g^{-1} soil was added for 50 kg N ha^{-1}

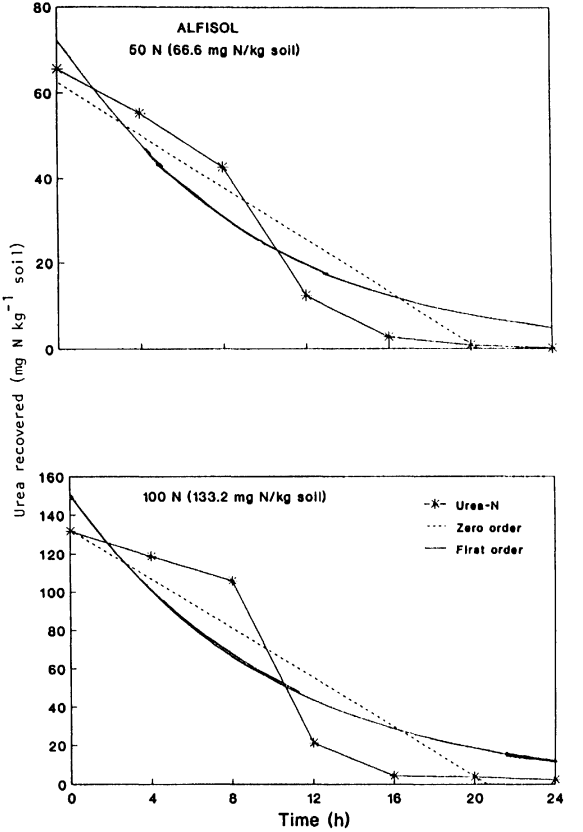


Figure 29: Exp.5: Disappearance of urea-N from 0-5 cm, soil samples after application of 66.6 and 133.2 mg N kg^{-1} soil as urea. The zero and first order relationships are:

50 N	:	Zero order	$Y = 62.6 - 3.08x$	$R^2 = 0.88$
		First order	$Y = 72.5e^{-0.11t}$	$R^2 = 0.92$
100 N	:	Zero order	$Y = 132.5 - 6.4x$	$R^2 = 0.83$
		First order	$Y = 150e^{-0.11t}$	$R^2 = 0.88$

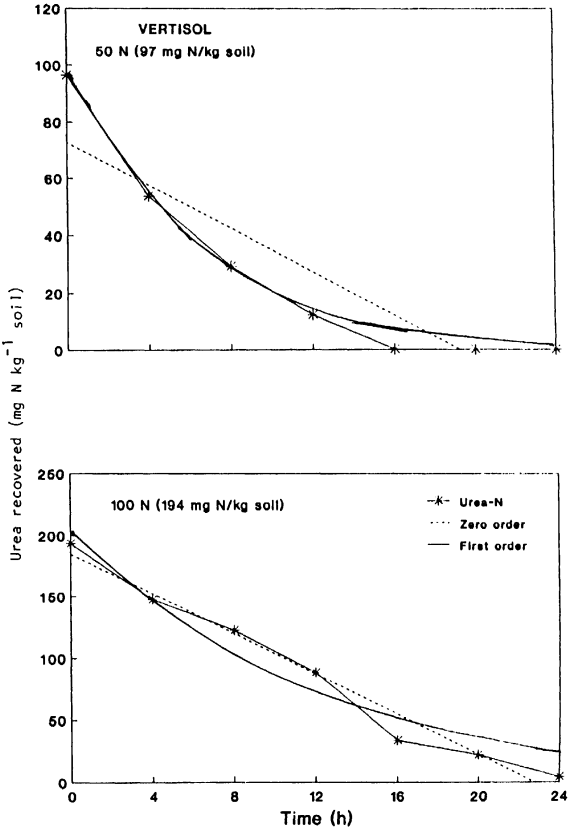


Figure 30: Exp.5: Disappearance of urea-N from 0-5 cm, soil samples after application of 97 and 194 mg N kg^{-1} soil as urea. The zero and first order relationships are:

50 N : Zero order $Y = 72.9 - 3.8x$ $R^2 = 0.78$

First order $Y = 98e^{-0.17t}$ $R^2 = 0.99$

100 N : Zero order $Y = 184.8 - 8.1x$ $R^2 = 0.97$

First order $Y = 204.3e^{-0.088t}$ $R^2 = 0.97$

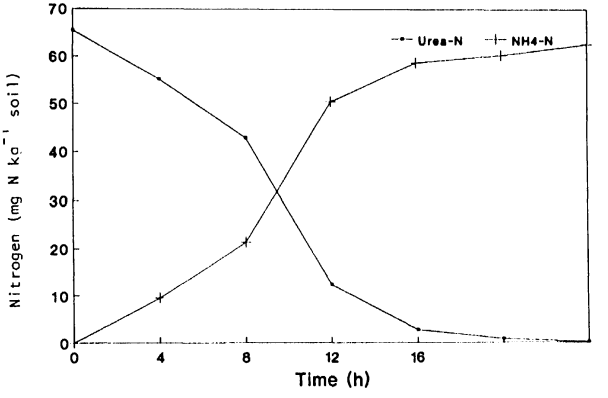


Figure 31: Exp.5: Urea derived inorganic nitrogen in the Alfisol, after application of 66.6 mg N kg^{-1} soil.

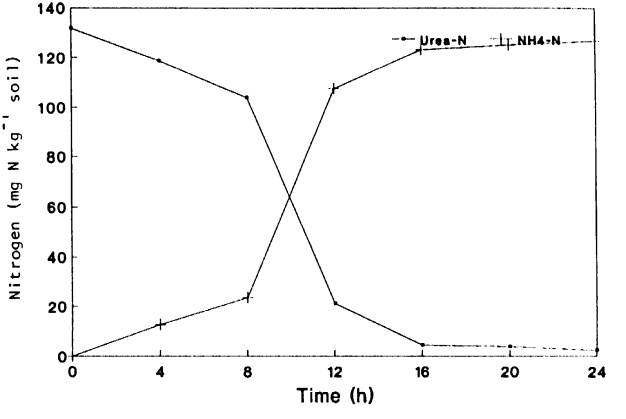


Figure 32: Exp.5: Urea derived inorganic nitrogen in the Alfisol, after application of 133.2 mg N kg^{-1} soil.

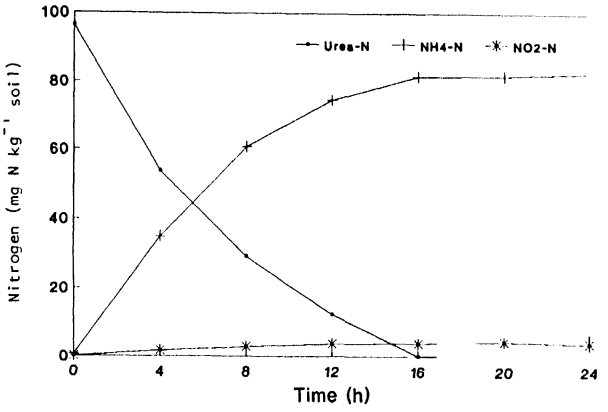


Figure 33: Exp.5: Urea derived inorganic nitrogen in the Vertisol after application of 97 mg N kg^{-1} soil.

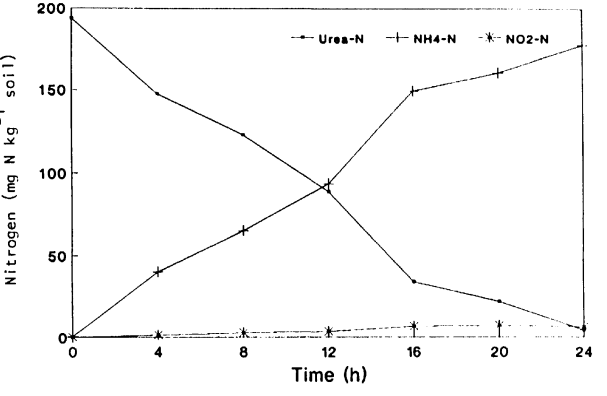


Figure 34: Exp.5: Urea derived inorganic nitrogen in the Vertisol after application of 194 mg N kg^{-1} soil.

(Appendix U) and 98 per cent in the 100 N treatment (Appendix V). In three two treatments NH_4^+-N was 95-96 per cent and NO_2^--N was 3-4 per cent in the inorganic nitrogen derived from urea-N.

4.2 UREA HYDROLYSIS HALF TIME VALUES (T 1/2) OBSERVED IN THE ALFISOL AND VERTISOL

To have comprehensive information of the rapidity of urea hydrolysis in the Alfisol and Vertisol, the time required in hours for hydrolysis of 50 per cent of added urea-N (as in the field experiments 1 and 2) or from urea-N recovered in zero hour samples (as in the microplot and incubation experiments) were calculated using urea hydrolysis rates of first order reaction kinetics. These values are denoted as T 1/2 or half time values and presented in Table 23 for the Alfisol and in Table 24 for the Vertisol along with urea hydrolysis rates of the first order reaction.

In all the field experiments it was observed that T 1/2 values were less in the Vertisol than for the Alfisol especially in the experiments in which solid urea was applied to the soil surface. While in the experiment 1 the difference in the T 1/2 value between the Alfisol and Vertisol was > 9.5 hours, in the 2 field experiment half time values in the Alfisol were nearly two times greater than the time required for hydrolysis of 50 per cent added urea-N in the Vertisol. The half time values of the microplot experiments were considerably less in the Alfisol and

Vertisol when compared to the field experiments 1 and 2. Also these values were close to each other in the Alfisol and Vertisol, the difference not exceeding more than 1 hour. However the T 1/2 values in the Vertisol were less than the half time values observed in the Alfisol in the 50 and 100 N treatments. The half time values for the Alfisol in the incubation experiment were higher than the values observed in the microplot experiments indicating a slower urea hydrolysis but in the Vertisol the T 1/2 values were inconsistent between the 50 and 100 N treatments. The time required to hydrolyse 50 per cent urea-N in the 100 N treatment in the Vertisol exceeded the half time values observed in the Alfisol for the same treatment.

Table 23. Urea hydrolysis rates (rate constants of the first order reactions) and half time (T 1/2) values (time required for 50% urea-N hydrolysis) in the Alfisol.

Type of experiment	Treatment	Organic carbon %	Bulk density g/cm^3	Clay %	Soil depth (cm)	Form of urea	Method of application	Experiment duration hours	Moisture % (W/W)	Temp °C	Rate constant(e) (% urea-N h^{-1})	T 1/2 h
Field plot ($4 m^2$)	100 N	0.35	1.31	20.4	0-15	Solid	Dry surface soil + irrigation	72	22.2-3.5	29.4 - 31.8(a)	2.4% h^{-1}	28.9
Field plot ($4 m^2$)	50 N	0.28	1.6	11.6	0-15	Solid	Moist surface	144	9.1-4.4	24.8 - 27.5(b)	0.91% h^{-1}	76.2
	100 N										1.1% h^{-1}	63.0
Field microplot ($38.5 cm^2$)	50 N	0.26	1.5	11.1	0-5	Urea solution	Mixed with moist soil	168	15.2-9.4	29.1 - 35.7(c)	13% h^{-1}	5.3
	100 N										15% h^{-1}	4.6
Field microplot ($38.5 cm^2$)	50 N	0.26	1.5	11.1	0-5	Urea solution	Mixed with moist soil	24	20-11.7	24-38(d)	13% h^{-1}	5.3
	100 N										12% h^{-1}	5.8
Incubation experiment	50 N	0.26	1.5	11.1	0-5	Urea solution	Added to air dried soil samples	24	24	32	11% h^{-1}	6.3
	100 N										11% h^{-1}	6.3

(a) Between 0717-1417 hours
(b) Between 0717-1417 hours
(c) Between 0930-1430 hours
(d) Between 1200-1200 hours
(e) Rate constant is shown as % urea-N hydrolysed per hour

Table 24. Urea hydrolysis rates (rate constants of the first order reactions) and half time (T 1/2) values (time required for 50% urea-N hydrolysis) in the Vertisol.

Type of experiment	Treatment	Organic carbon %	Bulk density g/cm^3	Clay %	Soil depth (cm)	Form of urea	Method of application	Experiment duration hours	Moisture % (W/W)	Temp °C	Rate constant (% urea-N h^{-1})	T 1/2 h
Field plot ($4 m^2$)	100 N	0.6	1.15	52.6	0-15	Solid	Dry surface soil + irrigation	72	23.2-16.2	29.4 - 31.8(a)	3.6% h^{-1}	19.25
Field plot ($4 m^2$)	50 N	0.42	1.1	51.3	0-15	Solid	Moist surface	144	23.2-18.0	24.8 - 27.5(b)	2.2% h^{-1}	31.5
	100 N										2.2% h^{-1}	31.5
Field microplot ($38.5 cm^2$)	50 N	0.39	1.03	50.0	0-5	Urea solution	Mixed with moist soil	168	35.9-28.5	31.7 - 36.4(c)	14% h^{-1}	5.0
	100 N										16% h^{-1}	4.3
Field microplot ($38.5 cm^2$)	50 N	0.39	1.03	50.0	0-5	Urea solution	Mixed with moist soil	24	46.7-33.9	24.5 - 41(d)	15% h^{-1}	4.6
	100 N										13% h^{-1}	5.3
Incubation experiment	50 N	0.39	1.03	50.0	0-5	Urea solution	Added to air dried soil samples	24	40	32	17% h^{-1}	4.1
	100 N										8.8% h^{-1}	7.9

(a) Between 0717-1417 hours
(b) Between 0717-1417 hours
(c) Between 0930-1430 hours
(d) Between 1200-1200 hours
(e) Rate constant is shown as % urea-N hydrolysed per hour

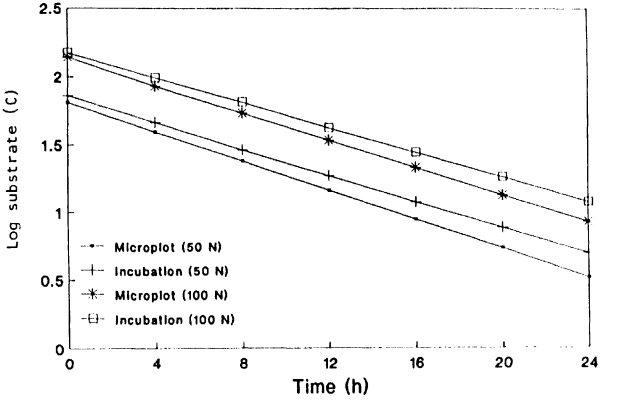


Figure 35: Relationship between concentration (C) of unhydrolysed urea-N and time for the short interval microplot and incubation experiments on the Alfisol.

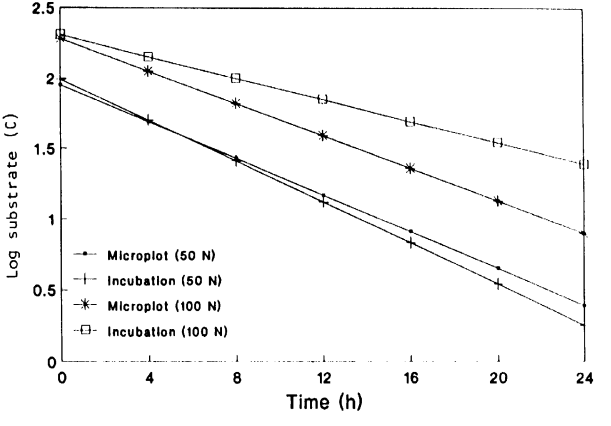


Figure 36: Relationship between log concentration (C) of unhydrolysed urea-N and time for the short interval microplot and incubation experiments on the Vertisol.

DISCUSSION

CHAPTER V

DISCUSSION

In these studies of urea hydrolysis, four field experiments and one laboratory experiment were conducted. Summaries of results are given in Tables 23, 24 and 25 to facilitate discussions on the different results obtained in these experiments.

5.1 METHODOLOGY

The series of the experiments conducted in the field represent stages in development of methodology for these studies on urea hydrolysis.

When urea was applied to the soil surface in the initial two experiments, recovery of hydrolysed urea as inorganic nitrogen in all treatments was very low between 36 and 65 per cent (Table 25). It appears that a substantial proportion of nitrogen was lost, presumably by volatilization of ammonia from the vicinity of partially disolved urea particles on the soil surface (see Section 5.5.4). Apart from the low recoveries, there were several other disadvantages in the methodology used for these two initial experiments. The moisture content of the surface soil decreased rapidly over the first 24 hours especially in the Alfisol (Figure 5) presumably due to both percolation and evaporation from the soil surface. The rapid changes in moisture content at the soil surface would directly affect the rate of urea hydrolysis, because of the effects of moisture content *per se*

(Sahrawat 1984). These changes in moisture, plus diurnal temperature fluctuations, posed difficulties in relating hydrolysis under varying environmental conditions in the field to the controlled conditions in the laboratory not only for these two initial experiments but also for any subsequent experiment.

To minimise changes in moisture content during experimentation, and to ensure that the soils would be at field capacity, it was decided to irrigate the soils thoroughly for several days before starting Experiments 3 and 4. To minimise moisture losses, the plots were covered with polyethlene sheets.

When urea had been spread on the soil surface, either before or after irrigation, the exact concentration in the soil was not known. Measurements only determined the average concentration in the depth sampled. Therefore, for making comparisons between field and laboratory studies, it was desirable for the urea to be uniformly mixed with a definite depth viz. 0-5 cm of surface soil. Substantial error can arise from uneven spreading of urea and sampling errors of the soils to recover this. Reduction of such error was desirable, so that maximum precision could be obtained for establishing the orders of reaction from the time series sampling. This was achieved by mixing urea in solution with the 0-5 cm depth of soil in the microplots, which were later destructively sampled including a zero-time sampling.

It has been common for confined microplots to be used whenever studies are made of the reactions of expensive materials with soil in the field, i.e. nitrogen fertilizers and organic matter labelled with N-15 or C-14. But such care is rare for studies of labile nitrogen components in the soil; In fact for studies of urea hydrolysis. no author has previously adapted this technique specifically to study urea hydrolysis in the field. The precision of the relationships from the field results obtained in Experiments 3 and 4 show the value of such a careful approach for urea hydrolysis studies with unlabelled fertilizer.

5.2. UREA MOVEMENT

It was desirable that movement of urea in the soil be minimised so that all changes in urea in a soil layer could be safely attributed to hydrolysis.

Invariably, almost all of the urea-N in the soil was present in the shallowest depth sampled, in both the Alfisol and the Vertisol (Tables 5, 6, 9, and 10). Even the wetting of the soil after urea application or application of urea to a moist soil did not cause appreciable movement of urea-N beyond the 15-cm depth in Experiment 1. In the microplot experiments, where urea in solution was mixed with soil from the 0-5 cm depth, the movement of urea beyond the 5 cm depth was less than 5 mg N kg^{-1} soil in the two soils.

Very little urea movement beyond the 10-cm depth in the was observed in the microplot experiments. These results are consistent with those from previous workers (McInnes et al., 1986; Savant et al., 1987b; Praveen-Kumar et al 1990). They found that the movement of urea-N into the soil was that expected from a non-ionic solute and was determined by the physical characteristics of the soil and quantity of water used for irrigation.

5.3 KINETICS OF UREA HYDROLYSIS

Many research workers have used the order of chemical reaction to describe the kinetics of urea hydrolysis. A zero order relationship was reported by Sahrawat (1980a) and Vlek and Carter (1983). Other research workers reported that urea hydrolysis in soil follows first order kinetics (Sankhayan and Shukla, 1976; Bajpai et al., 1984; Kumar and Wagnet, 1984; Yadav et al., 1987; Lindau et al., 1989). All this information came from laboratory experiments.

Under field conditions, in the present study, urea hydrolysis was usually described more accurately by the first order reaction than by a zero order reaction kinetics, indicating that urea hydrolysis rates were dependent on the concentration of urea and not just linear with time. Urea hydrolysis kinetics were very close to the first order reaction when urea was spread on to the soil surface either before or after irrigation (Figures 4, 7 and 8). But, in the Alfisol, the data also gave a good fit to the zero order

relationship (Figure 4) when urea application was followed by irrigation (Experiment 1). In the first microplot experiment when urea hydrolysis was rapid and almost complete in 24 hours (Experiment 3), there were insufficient measurements for accurate description of the order of reaction during hydrolysis of 95 per cent of the urea (Figures 15 and 16). But, in the subsequent microplot experiment (Experiment 4), when the short sampling intervals of 4 hours, were employed to study urea hydrolysis over 24 hours very good fits with first order kinetics were observed both in the Alfisol (Figure 22) and in the Vertisol (Figure 23). In the incubation experiment, urea hydrolysis also showed a good relationship with the first order reaction in both the Alfisol (Figure 29) and the Vertisol (Figure 30); however, for the 100 N treatment in the Vertisol (Figure 30) urea hydrolysis also gave a good fit to both zero and first order relationship.

In all the field experiments and in the incubation study, urea applied to the soils did not exceed 200 μg N g^{-1} soil. In many of the previous incubation experiments by other workers who also reported urea hydrolysis to be a first order reaction, urea-N added was also less than 200 μg g^{-1} soil. Sahrawat (1980a), who reported zero order kinetics for urea hydrolysis, applied 1000 μg N g^{-1} soil and used very short sampling intervals of 2 hours in his time-series measurements. The first order reactions observed in the field (Experiments 1 and 2), in which urea was applied to the surface of the soil, may be the result of the lower concentrations of urea-N

applied and gradual movement of urea to the deeper soil layers. Vlek and Carter (1983) reported a zero order reaction for urea hydrolysis, which they attributed to uniform distribution of urea in the soil matrix. In Experiments 3 and 4, mixing urea solution with the whole soil in the 0-5 cm depth in microplots did bring about the homogenous system described by Vlek and Carter (1983), but urea hydrolysis in both the 50 and 100 N treatments still followed a first order reaction more closely than a zero order reaction. Although not specifically studied, it is apparent that the method and form of urea application, environmental factors, and the individual characteristics of soils did not alter the reaction order of urea hydrolysis in the field. Sankhayan and Shukla (1976) also reported that soil properties do not modify the nature of the urea hydrolysis reaction.

5.4 UREA HYDROLYSIS RATES

The data on urea-N disappearence from the soil in all the experiments, especially those in the field, generally gave good fits with first order reaction kinetics. Hence urea hydrolysis rates are better reported by the urea hydrolysis rate constants. For convenience, these are expressed as per cent urea-N hydrolysed h^{-1} and additionally the half time (T 1/2) values were calculated. Both methods of expression are given in the summary of results for all the experiments are presented in Table 23 (Alfisol) and in Table 24 (Vertisol). Other workers have also used urea hydrolysis rate constants of the first order reaction and half time values (T 1/2) to

discuss the influence of organic matter (Bajpai et al., 1984), temperature and moisture (Yadav et al., 1987), and redox potential (Lindau et al., 1989) on urea hydrolysis.

5.4.1. Field Experiments

Urea hydrolysis rates measured in field varied markedly over the course of the experiments (0.9 to 15 per cent urea-N h^{-1}) in the Alfisol (Table 23) and (2.2 to 16 per cent urea N h^{1}) in the Vertisol (Table 24). These variations in urea hydrolysis rates can be attributed to the method of urea application, individual soil characteristics, and environmental factors such as moisture content and temperature. Although urea hydrolysis measured in the field reflects the integrated influence of the above mentioned factors, yet careful examination of the results brings out the influence of the some of these factors on urea hydrolysis.

It is difficult to compare these results from the field with the results (Table 3) from the field experiments conducted in other countries because of the different environmental factors and methods of urea application. The reports of (Malhi and Nyborg, 1979; Aulakh and Rennie 1984; Mohammed et al., 1984; McInnes et al., 1986) indicate urea hydrolysis was slow under temperate environments. Nevertheless, the results show that urea hydrolysis in the two SAT soils at ICRISAT Center was fast compared to some of the rates under temperate conditions.

5.4.1.1 Method of Urea Application

Urea hydrolysis observed in Experiments 1 and 2 was slow when solid urea was placed on the soil surface either before or after irrigation. It was consistently slower in both soils when urea was applied to the surface of moist soil than when it was leached into the soil (Tables 23 and 24). When urea in solution was mixed with the moist surface soil in the 0-5 cm depth in the microplot experiments, urea hydrolysis was very rapid in both the Alfisol and the Vertisol with rates of 15 and 16 per cent urea N h^{-1} respectively.

In general mixing urea with the soil appears to cause rapid urea hydrolysis in comparison to placing urea on the soil surface or banding. Malhi and Nyborg (1979) reported higher urea hydrolysis when it was mixed with the soil than banded at a depth of 5 cm (Table 3). Savant et al., 1987(b) described urea hydrolysis rates in the following sequence from the results of soil column studies; well mixed urea > surface applied urea (water added after) > surface applied urea (water added before). The hydrolysis rates of the field experiments conducted in the present study also fall into a similar sequence, with higher urea hydrolysis rates when urea in solution was mixed with soil. This confirms that soil urease activity was retarded when solid urea was applied to the soil surface.

5.4.1.2 Soils

Urea-N hydrolysis rates in the field were generally higher in the Vertisol than in the Alfisol. Sahrawat (1984) obtained similar results from laboratory incubations. These differences between soils in their urea hydrolysis rates can be attributed to soil characteristics such as organic carbon and clay content. Many workers, in India as well as other countries, have also reported higher urease activity in soils with increase in organic carbon content and higher clay content, with the most prominent being Dalal (1975a), Zantua et al., (1977), Sahrawat (1980b), Dash et al 1981, Bajpai et al., (1984).

5.4.1.3 Environmental Factors

Along with soil properties (especially organic matter and soil texture), and method of urea application, the rate of urea hydrolysis appears to have been affected by soil moisture and the temperature in the field experiments. It was difficult to distinguish between the effect of soil moisture and temperature on urea hydrolysis in the field, especially because both usually changed during an experiment. However, some observations give an indication of the possible importance of these factors on urea hydrolysis in the field.

When soil was made wet after urea application there was a sharp decline of moisture content in the 0-15 cm depth especially in the Alfisol between 2-24 hours (Figure 5). In this experiment the rapid loss of moisture from the surface

soil in the Alfisol through percolation and evaporation between 2 and 48 hours must have resulted in a lower urea hydrolysis rate, (Table 23) especially in comparison to the much smaller relative changes in soil water content in the Vertisol (Table 24).

In Experiment 2, where urea was applied to the moist surface soil, the decrease in moisture content in the soil surface was gradual in both the Alfisol and in the Vertisol. In the Alfisol, the moisture content in the 0-15 cm depth was only 9 per cent in the initial stages of the experiment (Figure 10) and decreased to 4.4 per cent in 144 hours. This low moisture content must have retarded the diffusion of urea causing low urea hydrolysis rate constants. In the Vertisol, wherein the moisture content in the surface soil decreased from 23 to 18 per cent between 2 and 144 hours urea hydrolysis rate constants were higher than in the Alfisol.

When urea solution was mixed with moist soil in the microplot experiments, the rate constants of the first order reaction were very high. Urea hydrolysis was very rapid and was essentially complete in 24 hours in both the soils.

These experiments show that hydrolysis of urea in Experiments 1 and 2 (surface applied urea) was considerably slower than hydrolysis in Experiments 3 and 4 when urea solution was mixed with the soil. The surface applied urea must reach the relatively stationary soil urease for hydrolysis to occur; according to Vlek and Carter (1983),

lack of free water in the soil may prevent diffusion of urea through soil and limit the contact between urea and soil urease. Savant et al. (1987b) observed slower urea hydrolysis of the surface applied urea than well mixed urea and attributed it to the mode and extent of urea transport and drying of the surface soil.

The temperature dependence of urease activity has been discussed by Overrein and Moe (1967), Dalal (1975), Bremner and Mulvaney (1978), Sahrawat (1984), Kumar and Wagnet (1984) and Gould et al. (1986). Vlek and Carter (1983) observed a linear relationship between temperature and the apparent rate constant of the zero order reaction (Ko) when moisture was not a limiting factor, over the temperature range of 10-40 ^{o}C. Yadav et al. (1987) have shown that rate constants of the first order reaction (K1) increased with the increase in temperature from 10 to 30^{o}C.

The results of the field experiments conducted in this study are in agreement with the observations made in the studies discussed above. In the experiment wherein urea was applied to the moist surface soil (Experiment 2), the low temperatures (Table 11) prevailed during the experimental period would be one of the factors for the low rate constants of the first order reaction in the Alfisol, and especially in the Vertisol where the moisture content was near 20 per cent even after 72 hours (Figure 10) and was not a great limiting factor for urea hydrolysis.

5.4.2 Laboratory Experiment

In the incubation experiment, urea-N hydrolysis rates were much greater than that those in the field experiments where urea was surface applied, but were similar to the rates when urea solution was mixed with the soil in the microplot experiments. Rates of hydrolysis were similar for the two rates of urea (50 and 100 N) in the Alfisol (Table 23). For the Vertisol, the 50 and 100 N treatments gave rates of 17 and 8.8 per cent urea-N hydrolysed h^{-1}. It is difficult to find a clear explanation for the contrasting hydrolysis rates observed in the Vertisol the 50 and 100 N treatments; by comparison with the results from other experiments, it appears that the rate obtained for the 100 N rate on the Vertisol is anomalously, low for an unknown reason.

Lower urea-N hydrolysis rates might have been expected in the incubation experiment, because of the air drying of field moist samples before grinding, sieving and rewetting. Zantua and Bremner (1977) reported an appreciable decrease in urease activity (9 to 33 per cent) due to air drying of moist soil and rewetting it during urease assay. They attributed this reduction to the release of urease from protected sites during air drying, and subsequent decomposition during rewetting and incubation.

5.4.3 Prediction of hydrolysis rates

Examination of the results from the incubation experiment and the microplot experiments show a remarkable closeness in

the urea hydrolysis rates with the hydrolysis rates being slightly lower in the incubation experiments (Tables 23 and 24). The closeness of the urea hydrolysis rates is illustrated by plotting the log of unhydrolysed urea-N concentration against time (Figures 35 and 36). The data therefore indicates that urea hydrolysis rates in the field can be predicted from the urea hydrolysis rates determined in the laboratory, because the soil moisture contents and temperature were approximately similar in both the experiments.

However, further detailed experimentation needs to be done, with particular attention to better monitoring of environmental variables like moisture and temperature. The effects of site variables like organic matter and clay content of the soils, and treatment of soils prior to incubation (e.g. air drying), need to be characterised.

5.5 UREA HYDROLYSIS PRODUCTS

Conversion of urea to NH_4^+-N reduces the possibility of leaching loss of urea before plants can absorb nitrogen because NH_4^+-N will be adsorbed onto the cation exchange complex. But subsequent nitrification to NO_2^--N and NO_3^--N gives the forms of nitrogen which are susceptible for further losses by leaching. Although it was not a primary aim of this study to assess the rate of NO_2^--N and NO_3^--N appearance, the data gives general useful information about these species during urea hydrolysis.

5.5.1 Ammonium-N

The increase in NH_4^+-N following application of urea to the dry soil surface and then irrigated was proportional to the disappearance of urea-N but it was not fully quantitative. (Figures 6 and 7). After 24 hours, NH_4^+-N accumulation accounted for only 61 per cent of urea-N disappeared in the Alfisol and 65 per cent in the Vertisol. (Table 25). This could be due to gaseous loss of NH_3 during urea-N hydrolysis from the surface applied urea, with perhaps some fixation of ammonium ion especially in the Vertisol.

The accumulation of NH_4^+-N in the Alfisol, was almost accounted for 60-70 per cent of the urea-N hydrolysed when urea was applied to the surface of moist soil. A part of NH_4-N was oxidised to NO_3^--N in the two treatments (Figures 11 and 12) This build up of NH_4^+-N continued upto 96 hours and later decreased as it was oxidised to NO_3^--N. The NH_4^+-N accumulation in the soil bore a better relationship with urea-N hydrolysis in this experiment than when urea was applied to dry soil.

In the two microplot experiments (in which urea was mixed with the soil), and in the incubation experiment, a rapid increase in NH_4^+-N concentration within 24 hours was very closely associated with urea-N hydrolysis as over 90 per cent of urea-N hydrolysed was recovered as NH_4^+-N, and most of the recoveries were in the range of 96-100 per cent.

Loss of ammonia from surface applied urea was reported earlier (Overrein and Moe, 1967; Delaune and Patrick 1970). Hydrolysed urea-N could have been lost as ammonia due to volatilization, or fixed by clay or organic matter (Sahrawat 1979).

5.5.2 Nitrite-N

The concentrations of NO_2^--N were naturally very small (less than 0.5 mg N kg^{-1} soil) in the Alfisol (Tables 16 and 20). But, in the Vertisol, the NO_2^-N accumulated to much high levels; in both the 0-5 and 5-10 cm depths in the first microplot experiments (Figures 20 and 21) and reached a peak of over 10 mg N kg^{-1} in the 0-5 cm depth after 72 hours of urea application.

In the incubation experiment, where the air dried soil samples from moist fields were used, small amounts (upto 7 mg N kg^{-1} soil) of NO_2^-N were observed. Magalhaes et al. (1987) and Kumar et al. (1988) observed that a soil reaction of greater than pH 8 (Table 6) and high concentrations of NH_4^+ ions following urea-N hydrolysis, could promote NO_2^--N accumulation.

5.5.3 Nitrate-N

Very small amounts (< 3 mg N kg^{-1} soil) of NO_3^--N accumulated in the Alfisol and Vertisol in 72 hours, after application of urea to soil surface followed by irrigation. In experiments which were conducted for 144 and 168 hours,

there was a steady accumulation of NO_3^--N in the Alfisol and the Vertisol. In 2 and 3 experiments, the build up of NO_3^-N began between 72 and 96 hours after urea application and continued to increase until the termination of the experiments. The oxidation of NH_4^+-N was less in the Alfisol than in the Vertisol and this may be due to the low pH of the Alfisol, which was below 6 (Tables 4 and 8). Sahrawat (1982); Magalhaes et al. (1987) observed highest oxidation of NH_4^+-N to NO_3^--N in soils with a pH of 6 and above.

5.5.4 Recovery of Urea-N Hydrolysed

Over all the experiments, the recovery of hydrolysed urea-N in the inorganic forms of NH_4^--N, NO_2^--N, and NO_3^--N was incomplete. The data presented in the Table 25 for all the experiments conducted in this study show the recovery of inorganic forms of nitrogen was good , when urea solution was mixed with moist soil in the microplot experiments and in the incubation experiment. Recoveries of between 93 and 100 per cent for the microplot experiments (Table 25) must be considered as extremely good for field results. But the recoveries of 36 to 65 per cent when urea was applied to a dry or moist soil surface (Table 25) indicate substantial losses of nitrogen. Also, the higher recovery of inorganic nitrogen when urea was applied to dry soil and leached into the soil (61-65 per cent) than when it was applied to the surface of moist soil (36-54 per cent) indicate greater losses in the latter treatment.

These low recoveries of inorganic Nitrogen in the Experiments 1 and 2 must have been due to Volatilization of ammonia during hydrolysis of surface applied urea in the uncovered plots. Volatilization is known to occur when urea is placed on the soil surface and the soil surface is alkaline either naturally (Vertisol) or due to a pH increase during urea hydrolysis (Alfisol) and losses are promoted by drying of the surface soil.

Table 25. Recoveries (%) of inorganic nitrogen from urea hydrolysed in 24 hours in the Alfisol and Vertisol.

Method of urea application	Soil depth (cm)	Urea-N ($kg\ ha^{-1}$)	Inorganic nitrogen recovered as NH_4^+, NO_2^- and NO_3^-N	
			Alfisol	Vertisol
Crystalline urea surface application before wetting	0-30	100 N	61	65
Crystalline urea surface application to moist soil	0-30	50 N	36	42
	0-30	100 N	53	54
Urea solution mixed with soil	0-10	50 N	93	98
	0-10	100 N	99	99
Urea solution mixed with soil	0-10	50 N	97	96
	0-10	100 N	98	100
Incubation Experiment urea solution added to soil	0-10	50 N	96	90
	0-10	100 N	98	98

5.6 CONCLUSIONS

The experiments conducted on the benchmark Alfisol and Vertisol at the ICRISAT Center have given an insight into urea hydrolysis under the ambient environmental conditions of semi-arid tropics. Investigations in the field have given information about urea hydrolysis in a dynamic system which exists in the field that is, the changing soil moisture contents, the diurnal fluctuations of air and soil temperatures, and the pH changes in the soil following urea application.

Urea hydrolysis was rapid in both soils under field conditions. Almost all the urea applied (50 and 100 kg N ha^{-1}) hydrolysed within 24 hours of application, when soil moisture content was near field capacity, soil temperatures were between 27-37^{o}C, and the urea was mixed well with the soil. Urea hydrolysis was comparatively slow when urea was applied to the soil surface, particularly when it was moist and there was no subsequent precipitation to leach the nitrogen into the soil.

In the field experiments urea hydrolysis rates were greater in the Vertisol than in the Alfisol. These results confirm Sahrawat's (1984) findings from incubation experiments.

Urea hydrolysis kinetics in the field obeyed first order reaction kinetics. The nature of the reaction was independent of the soil properties, the method of urea application, and

the influence of the environmental factors.

Because, urea hydrolysis rates and half time values (T 1/2) in the incubation and microplot experiments were very similar (Figures 35 and 36, Tables 23 and 24), it appears that the laboratory incubation experiments can be used for predicting the hydrolysis rates in the field, provided that similar conditions of temperature and moisture are used.

Measurements of the products of urea hydrolysis were useful for identifying substantial loss of nitrogen from surface applied urea, but not urea that was incorporated into the soil.

Although this study was undertaken primarily to ascertain the feasibility of using hydrolysis rates in the laboratory for predicting rates in the field, the results are of immediate practical significance. First, urea hydrolysis is so rapid that urea incorporated into moist soil at normal rates of application will be hydrolysed within a day of application, and so will be safe from leaching after that time. Second, surface applications clearly cause substantial loss of nitrogen within a short time and urea incorporation into the soil is essential to minimise such losses.

This thesis has primarily shown that the results from the laboratory experiments can predict urea hydrolysis rates in the fields of the Alfisol and Vertisol if due allowance is made for environmental factors such as temperature and

moisture content. However, application of these results depends upon further developments. Experimentation is required to relate urea hydrolysis quantatively to environmental variables such as soil temperature and soil moisture and to site variables such as organic matter and clay content. The effect of preparation of soil sample for laboratory incubation also needs to be characterised. This should allow the present data from the ICRISAT Center to be used to modify general models for predicting nitrogen behaviour in soils.

SUMMARY

CHAPTER VI

SUMMARY

Urea applied to soil is vulnerable to leaching if its application is immediately followed by heavy rain or irrigation before it can be hydrolysed to NH_4^+-N. Very few investigators have studied urea hydrolysis in the field, and no precise methods have been developed to measure urea hydrolysis in the field. The lack of information on urea hydrolysis rates in the field is particularly noticeable for semi-arid tropical environments such as those that cover much of India. This study was therefore undertaken to measure urea hydrolysis in the field on the benchmark Alfisol and Vertisol at ICRISAT Center, and to determine whether urea hydrolysis rates in the field could be predicted from the hydrolysis rates determined in laboratory experiments.

Four field and one incubation experiments were conducted. In the first field experiment, urea was spread on to the soil surface of 4 m^2 plots, which were then irrigated and the course of urea hydrolysis studied by sampling the soil and analysing for unhydrolysed urea over 72 hours. In the Experiment 2, urea was applied to the surface of moist soil and urea hydrolysis was studied in a similar fashion for 144 hours. In the subsequent experiments, urea in solution was mixed with soil from the 5 cm depth in small microplots which were covered with polyethylene sheets, and hydrolysis was determined by destructive sampling analysis of individual microplots. Urea hydrolysis was measured at 24 hours

intervals over a total period of 168 hours in Experiment 3, and for 24 hours in Experiment 4 with short sampling intervals of 4 hours. Finally, urea hydrolysis was studied in incubation experiments in the laboratory under controlled conditions. Urea in solution was added to samples of air-dry soil collected from the 5 cm depth of soil from the field experiments and were incubated at constant moisture (field capacity) and temperature (32^{o}C) for 24 hours, with short sampling intervals of 4 hours for determining urea hydrolysed. In all the field experiments urea was applied at the rate of 50 and 100 kg N ha^{-1}, except in Experiment 1 in which a rate of only 100 kg ha^{-1} N was used.

In all these experiments, urea hydrolysis fitted the relationship for a first order reaction better than that for a zero order reaction.

Urea hydrolysis was rapid in both the Alfisol and Vertisol. However, urea hydrolysis was much slower when urea was applied to the soil surface in the first two experiments (0.9-3.6 per cent urea-N h^{-1}) than when mixed with moist soils in the microplot experiments (12-16 per cent urea-N h^{-1}). In both the microplot and incubation experiments, more than 90% of the applied urea was hydrolysed within 24 hours.

Urea hydrolysis rates in all the field experiments were higher in the Vertisol than in the Alfisol. When urea was applied to the surface of moist soil (Experiment 2), the urea hydrolysis in the Vertisol was twice as fast as in the

Alfisol. But, the differences in urea hydrolysis rates between the Alfisol and Vertisol were small in the microplot experiments.

Urea hydrolysis rates in the microplot experiments were generally similar to those in the laboratory incubation experiment.

The microplot method of experimentation with destructive sampling method appears to be a more precise technique for studying urea hydrolysis under field conditions. This conclusion is based on the better recovery of unhydrolysed urea and inorganic forms of nitrogen in the microplot experiments (90-100 percent) than in experiments in which urea was applied to the soil surface (36-65 per cent). The lower recovery indicates that losses of nitrogen may occur from urea applied to the soil surface.

This study reveals several implications for future work. First, it shows that urea hydrolysis rates can be measured accurately in the field, and that these rates were similar to those measured under somewhat similar conditions in the laboratory. Therefore it appears feasible that hydrolysis rates in the field can be predicted from laboratory assays. But for such predictions for field situation, careful consideration must be given to the environmental variables such as moisture and temperature which have such a large influence on urea hydrolysis. Further studies are therefore needed to carefully quantify the relationship between

hydrolysis rate and temperature and moisture for a particular soil.

Soils usually have a distinct hydrolysis rate that is governed mainly by their organic matter and clay content: if the relationship between these soil characteristics and urea hydrolysis can be determined for major soils, the urea hydrolysis rates can perhaps be predicted from soil properties and the prevailing environmental conditions. Such work could reduce the need for urea hydrolysis measurements. The information generated from such an approach could be useful in modifying models that generally describe the behavior of nitrogen in soils to be more appropriate for Indian conditions.

Two important practical aspects have emerged from this study. The first one is that in the Alfisol and Vertisol the hydrolysis of urea was very fast and most of the urea applied hydrolysed within 24 hours after incorporation into soil that was moist. Thus, urea fertilizer would be susceptible for leaching for less than a day. Secondly loss of nitrogen occurred when urea was placed on the surface of moist soil. Consideration must therefore be given to the split methods for applying urea. The conventional improved method of applying fertilizer urea by split or fractional application, located below the soil surface appears to be beneficial in increasing the fertilizer use efficiency of urea. The spreading of urea on the soil surface is not uncommon, especially for topdressing. Thus, there is need to encourage incorporation of urea into the soil.

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Appendix A. Experiment I: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations (kg ha^{-1}) in an Alfisol in the field: following application of 100 kg urea N ha^{-1}.

	Time (h)			
	2	24	48	72
Surface soil 0-15 (a)				
Urea-N	-8.4	-36.5	-73.3	-84.5
NH_4^+-N	2.2	22.2	34.2	44.4
NO_2^--N	0.02	0.04	0.02	0.12
NO_3^--N	-1.0	-0.4	2.0	3.1
Sub surface soil 15-30 cm (b)				
Urea-N	0	0	0	0
NH_4^+-N	0.6	0.2	0	-0.2
NO_2^--N	0.04	0	0.04	0.04
NO_3^--N	1.0	0.4	0.2	-0.2
Total depth 0-30 cm (a+b)				
Urea-N hydrolysed	8.4	36.5	73.3	84.5
Urea hydrolysis products recovered in 0-30 cm soil				
NH_4^+-N	2.8	22.4	34.2	44.2
NO_2^--N	0.06	0.04	0.06	0.16
NO_3^--N	0	0	2.2	2.9
Total	2.9	22.4	36.5	47.3
Nitrogen not recovered	5.5	14.1	36.8	37.2
As % of applied N	(66)	(39)	(50)	(44)

Appendix B. Experiment I: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations (kg ha^{-1}) in a Vertisol in the field: following application of 100 kg urea-N ha^{-1}.

Soil depth cm	Time (h) 2	24	48	72
Surface soil 0-15 cm (a)				
Urea-N	-16.0	-68.5	-76.9	-80.9
NH_4^+-N	5.9	38.3	43.6	46.6
NO_2^--N	0.03	0.05	0.12	0.12
NO_3^--N	-0.5	-2.9	3.1	2.4
Subsurface soil 15-30 cm (b)				
Urea-N	0	0	0	-1.8
NH_4^+-N	0.4	1.4	0.8	-0.2
NO_2^--N	-0.02	-0.02	0.02	0.02
NO_3^--N	0.4	2.1	0.2	-0.8
Total depth, 0-30 cm (a+b)				
Urea-N hydrolysed	16	68.5	76.9	82.7
Urea hydrolysis products recovered in 0-30 cm soil				
NH_4^+-N	6.3	39.7	44.4	46.4
NO_2^--N	0.01	0.03	0.14	0.14
NO_3^--N	-0.1	5.0	3.3	1.6
Total	6.2	44.7	47.8	48.1
Nitrogen not recovered	9.8	23.81	29.1	34.6
As % of applied N	(61)	(35)	(38)	(43)

Appendix C. Experiment 1: Weather data recorded at ICRISAT meteorology observatory during conduct of experiment 1, 17-20 October 1986

Date	Rain mm	Evapo mm	Air temp (°C)		Rel humidity %		Wind $Km\ h^{-1}$	Sunshine h	Sol rad tion
1986			Max	Min	0717	1417			MJM2/d
Oct 17	0	6.6	34.0	22.5	77.0	34.0	8.6	9.5	18.4
18	0	7.3	34.5	20.6	82.0	24.0	7.6	9.4	18.3
19	0	7.4	34.0	17.5	81.0	25.0	9.4	10.0	17.9
20	0	7.4	32.0	17.4	77.0	26.0	9.0	11.0	18.2
Mean		7.2	33.6	19.5	79.3	27.3	8.7	9.9	18.2

Appendix D: Experiment 2: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations (kg/ha^{-1}) in an Alfisol in the field: following application of 50kg urea-N ha^{-1}.

	Time (h)						
	2	24	48	72	96	120	144
Surface soil 0-15 cm (a)							
Urea-N	-6.0	-13.2	-21.6	-25.0	-28.1	-33.6	-38.4
NH_4^+-N	1.9	4.8	12.7	17.5	20.6	20.9	27.8
NO_2-N	0	0.02	0.05	0.07	0.05	0.12	0.0
NO_3-N	-0.5	0.5	1.2	1.0	1.9	4.1	5.5
Subsurface soil 15-30 cm (b)							
Urea-N	0	0	0	0	0	0	0
NH_4^+-N	-1.0	0.2	0	-0.2	0.7	1.2	0.5
NO_2-N	0	-0.05	0.07	0.02	0.1	0.05	0
NO_3-N	-1.2	-0.7	-0.7	0.7	1.4	1.2	0.7
Total depth, 0-30 cm (a+b)							
Urea-N hydrolysed	6.0	13.2	21.6	25.0	28.1	33.6	38.4
Urea hydrolysis products recovered in 0-30 cm soil							
NH_4^+-N	0.9	5.0	12.7	17.3	21.3	22.1	28.3
NO_2-N	0	-0.03	0.12	0.09	0.15	0.17	0.02
NO_3-N	-1.7	-0.2	0.5	1.7	3.3	5.3	6.2
Total	-0.8	4.8	13.3	19.1	24.8	27.5	34.5
Nitrogen not recovered	6	8.4	8.3	5.9	3.3	6.1	3.9
As % of applied N	(100)	(64)	(38)	(24)	(12)	(18)	(10)

Appendix E: Experiment 2: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations (kg ha^{-1}) in an Alfisol in the field: following application of 100 kg urea N ha^{-1}

	Time (h)						
	2	24	48	72	96	120	144
Surface soil 0-15 cm (a)							
Urea-N	-7.2	-25	-30.7	-57.4	-66.2	-73.9	-80.6
NH_4^+-N	4.1	13.0	20.2	37.2	41.0	45.6	56.6
NO_2-N	0.07	0.05	0.19	0.12	0.17	0.17	0.17
NO_3-N	0.5	0.2	2.6	1.4	1.9	6.7	10.1
Subsurface soil 15-30 cm (b)							
Urea-N	0	0	-0.7	-0.7	-0.7	-0.7	-0.7
NH_4^+-N	-1.2	-0.2	0	-0.7	1.0	0.2	0.5
NO_2-N	0.07	-0.5	0.1	0.12	0.3	0.3	0.6
NO_3-N	0.3	0.3	0.6	-0.2	1.2	1.7	1.7
Total depth, 0-30 cm (a+b)							
Urea-N hydrolysed	7.2	25	31.4	58.1	66.9	74.6	81.3
Urea hydrolysis products recovered in 0-30 cm soil							
NH_4^+-N	2.9	12.8	20.2	36.5	42.0	45.8	57.1
NO_2-N	0.14	0	0.29	0.24	0.47	0.47	0.77
NO_3-N	0.8	0.5	3.2	1.2	3.1	8.4	11.8
Total	3.8	13.3	23.7	37.9	45.6	54.7	69.7
Nitrogen not recovered	3.4	11.7	7.7	20.2	21.3	19.9	11.6
As % of applied N	(47)	(47)	(25)	(35)	(32)	(27)	(14)

Appendix F. Experiment 2: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations (kg ha^{-1}) in a Vertisol in the field: following application of 50 kg urea-N ha^{-1}.

	Time (h)						
	2	24	48	72	96	120	144
Surface soil 0-15 cm (a)							
Urea-N	-11.1	-25.9	-31.5	-41.6	-43.1	-48.3	-48.5
NH_4^+-N	4.6	9.9	15.0	23.6	28.1	22.4	16.3
NO_2-N	-0.07	-0.03	0.08	0.12	0.17	-0.05	0.13
NO_3-N	-1.5	-0.2	-0.5	1.5	0.2	8.3	15.5
Subsurface soil 15-30 cm (b)							
Urea-N	0	0	0	0	0	0	0
NH_4^+-N	-0.2	0.2	0	0.2	0.2	0.4	0.5
NO_2-N	-0.05	0.07	0.02	0.11	-0.02	-0.07	-0.15
NO_3-N	0.7	1.1	0.4	0.7	-0.2	3.6	5.4
Total depth, 0-30 cm (a+b)							
Urea-N hydrolysed	11.1	25.9	31.5	41.6	43.1	48.3	48.5
Urea hydrolysis products recovered in 0-30 cm soil							
NH_4^+-N	4.4	10.1	15.0	23.8	28.3	22.8	16.8
NO_2-N	-0.12	0.04	0.1	0.23	0.15	-0.12	-0.02
NO_3-N	-0.8	0.9	-0.1	2.2	0	11.9	20.9
Total	3.5	11.0	15.0	26.2	28.5	34.6	37.7
Nitrogen not recovered	7.6	14.9	16.5	15.4	14.6	13.7	10.8
As % of applied N	(67)	(58)	(52)	(37)	(34)	(28)	(22)

Appendix G. Experiment 2: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations (kg ha^{-1}) in a Vertisol in the field: following application of 100 kg urea N ha^{-1}.

	Time (h)						
	2	24	48	72	96	120	144
Surface soil 0-15 cm (a)							
Urea-N	-14.7	-47.9	-66.3	-75.1	-91.9	-93.4	-95.4
NH_4^+-N	7.4	25.1	36.1	49.3	65.2	55.1	50.0
NO_2-N	-0.04	0.02	0.13	0.1	0.2	0.1	0.4
NO_3-N	0.3	0	2.3	1.8	1.0	13.5	19.5
Subsurface soil 15-30 cm (b)							
Urea-N	0	0	0	0	0	0	0
NH_4^+-N	-0.4	-0.4	0	0.9	0.4	0.5	0.5
NO_2-N	-0.02	0.09	0.04	0.02	0.04	0.05	-0.09
NO_3-N	0.9	0.9	2.2	1.6	3.1	4.0	5.4
Total depth, 0-30 cm (a+b)							
Urea-N hydrolysed	14.7	47.9	66.3	75.1	91.9	93.4	95.4
Urea hydrolysis products recovered in 0-30 cm soil							
NH_4^+-N	7.0	24.7	36.1	50.2	65.6	55.6	50.5
NO_2-N	-0.06	0.11	0.17	0.12	0.24	0.15	0.31
NO_3-N	1.2	0.9	4.5	3.4	4.1	17.5	24.9
Total	8.1	25.7	40.8	53.7	69.9	73.3	75.7
Nitrogen not recovered	6.6	22.2	25.5	21.4	22.0	20.1	19.7
As % of applied N	(45)	(46)	(39)	(29)	(24)	(22)	(21)

Appendix H. Experiment 2: Weather data recorded at ICRISAT meteorology observatory during conduct of experiment 2, 17-23 December 1986

Date	Rain mm	Evapo mm	Air temp (°C)		Rel humidity %		Wind Kh-1	Sunshine h	Sol radiation
1986			Max	Min	0717	1417			MJM2/day
Dec 17	0	5.9	30.0	17.2	89.0	33.0	9.7	9.8	16.8
18	0	7.3	30.0	13.0	96.0	30.0	11.3	10.5	18.3
19	0	5.8	29.2	15.5	88.0	27.0	9.2	10.5	18.3
20	0	6.0	29.0	16.5	92.0	38.0	8.8	10.5	17.7
21	0	6.0	29.0	15.2	89.0	37.0	7.9	10.5	17.5
22	0	4.1	29.0	14.2	94.0	44.0	6.7	10.3	16.5
23	0	4.7	28.5	15.6	96.0	37.0	7.3	10.3	17.4
Mean		5.7	29.2	15.3	92.0	35.1	8.9	10.3	17.5

Appendix I. Experiment 3: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations (kg ha^{-1}) in an Alfisol in the microplot: following application of 50 kg urea-N ha^{-1}.

	Time (h)						
	24	48	72	96	120	144	168
Surface soil 0-5 cm (a)							
Urea-N	-45.9	-47.2	-47.9	-47.9	-47.9	-47.9	-47.9
NH_4^+-N	39.5	38.5	38.9	33.9	29.7	23.6	20.4
NO_2^--N	0	0	0.01	0.02	0.01	0	0
NO_3^--N	0.3	0.5	0.8	2.5	5.9	8.9	11.8
Subsurface soil 5-10 cm (b)							
Urea-N	-0.2	-0.8	-0.8	-0.8	-0.8	-0.8	-0.8
NH_4^+-N	2.2	3.5	4.1	3.2	3.5	2.9	2.9
NO_2^--N	0.01	0	0.01	0	0	0	0
NO_3^--N	0.8	0.5	0.2	1.0	1.7	3.8	4.7
Total depth, 0-10 cm (a+b)							
Urea-N hydrolysed	46.1	48.0	48.7	48.7	48.7	48.7	48.7
Urea hydrolysis products recovered in 0-10 cm soil							
NH_4^+-N	41.7	42.0	43.0	37.1	33.2	26.5	23.3
NO_2^--N	0.01	0	0.02	0.02	0.01	0	0
NO_3^--N	1.1	1.0	1.0	3.5	7.6	12.7	16.5
Total	42.8	43.0	44.0	40.6	40.8	39.2	39.8
Nitrogen not recovered	3.3	5.0	4.7	8.1	8.7	9.5	8.9
As % of applied N	(7)	(10)	(10)	(17)	(18)	(20)	(18)

Appendix J. Experiment 3: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations (kg ha^{-1}) in an Alfisol in the microplots: following application of 100 kg urea-N ha^{-1}.

	Time (h)						
	24	48	72	96	120	144	168
Surface soil 0-5 cm (a)							
Urea-N	93.3	-95.4	-95.7	-95.7	-95.7	-95.7	-95.7
NH_4^+-N	81.8	81.0	75.7	70.8	66.9	55.4	54.2
NO_2^--N	0	0.02	0.02	0.05	0	0	0
NO_3^--N	-0.1	0.3	-0.1	3.8	5.3	15.1	17.0
Subsurface soil 5-10 cm (b)							
Urea-N	0	-0.3	-0.8	-0.8	-0.8	-0.8	-0.8
NH_4^+-N	9.7	10.7	9.3	8.5	7.9	7.6	6.3
NO_2^--N	0.01	0.01	0	0	0	0	0
NO_3^--N	0.6	0.4	0.1	1.8	3.8	5.2	5.5
Total depth, 0-10 cm (a+b)							
Urea-N hydrolysed	93.3	95.7	96.5	96.5	96.5	96.5	96.5
Urea hydrolysis products recovered in 0-10 cm soil							
NH_4^+-N	91.5	91.7	85.0	79.3	74.8	63.0	60.5
NO_2^--N	0.01	0.03	0.02	0.05	0	0	0
NO_3^--N	0.5	0.7	0	5.6	9.1	20.3	22.5
Total	92.0	92.4	85.0	85.0	83.9	83.3	83.0
Nitrogen not recovered	1.3	3.3	11.5	11.5	12.6	13.2	13.5
As % of applied N	(1)	(3)	(12)	(12)	(13)	(14)	(14)

Appendix K. Experiment 3: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations (kg ha^{-1}) in a Vertisol in the microplot: following application of 50 kg urea N ha^{-1}.

	Time (h)						
	24	48	72	96	120	144	168
Surface soil 0-5 cm (a)							
Urea-N	-44.7	-45.2	-45.5	-45.7	-46.0	-46.0	-46.0
NH_4^+-N	40.0	36.6	34.9	30.9	27.7	24.3	22.8
NO_2^--N	1.4	3.2	4.4	3.7	2.8	2.4	1.9
NO_3^--N	-0.1	-0.4	-0.9	3.3	6.7	9.0	10.4
Subsurface soil 5-10 cm (b)							
Urea-N	0	0	-0.1	-0.2	-0.2	-0.2	-0.2
NH_4^+-N	2.0	2.9	2.3	2.2	1.8	1.5	1.3
NO_2^--N	0.8	1.4	1.8	1.3	1.0	0.8	0.8
NO_3^--N	-0.2	-0.3	0.2	1.8	2.8	3.1	3.6
Total depth, 0-10 cm (a+b)							
Urea-N hydrolysed	44.7	45.2	45.6	45.9	46.2	46.2	46.2
Urea hydrolysis products recovered in 0-10 cm soil							
	42.0	39.5	37.2	33.1	29.5	25.8	24.1
	2.2	4.6	6.2	5.0	3.9	3.2	2.7
	-0.3	-0.7	-0.7	5.1	9.7	12.1	14.0
Total	43.9	43.4	42.7	43.2	43.1	41.1	40.8
Nitrogen not recovered	0.8	1.8	2.9	2.7	3.1	5.1	5.4
As % of applied N	(2)	(4)	(6)	(6)	(7)	(11)	(12)

Appendix L. Experiment 3: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations (kg ha^{-1}) in a Vertisol in the microplots: following application of 100 kg urea-N ha^{-1}.

	Time (h)						
	24	48	72	96	120	144	168
Surface soil 0-5 cm (a)							
Urea-N	-92.5	-92.9	-93.5	-93.7	-94.3	-94.4	-94.4
NH_4^+-N	84.7	79.4	79.2	70.2	61.9	58.0	52.4
NO_2^--N	2.0	4.9	5.4	4.3	4.1	3.5	2.1
NO_3^--N	0.4	0.2	0.7	5.6	11.6	15.1	22.0
Subsurface soil 5-10 cm (b)							
Urea-N	0	0	-0.1	-0.2	-0.2	-0.2	-0.2
NH_4^+-N	3.6	3.8	2.8	3.3	2.4	2.0	1.8
NO_2^--N	0.9	3.2	3.2	2.2	1.3	1.0	0.9
NO_3^--N	0.1	0.5	0.1	2.4	3.6	4.3	5.6
Total depth, 0-10 cm (a+b)							
Urea-N hydrolysed	92.5	92.9	93.6	93.9	94.5	94.6	94.6
Urea hydrolysis products recovered in 0-10 cm soil							
NH_4^+-N	88.3	83.2	82.2	73.5	64.3	60.0	54.2
NO_2^--N	2.9	8.1	8.6	6.5	5.4	4.5	3.0
NO_3^--N	0.5	-0.7	-0.8	8.0	15.2	19.4	27.6
Total	91.7	90.6	89.8	88.0	84.9	83.9	84.8
Nitrogen not recovered	0.8	2.3	3.8	5.9	9.6	10.7	9.8
As % of applied N	(1)	(3)	(4)	(6)	(10)	(11)	(10)

Appendix M. Experiment 3: Weather data recorded at ICRISAT meteorology observatory during conduct of experiment 3, 23-31 October 1987.

Date 1987	Rain mm	Evapo mm	Air temp (°C) Max	Air temp (°C) Min	Rel humidity % 0717	Rel humidity % 1417	Wind Kh-1	Sunshine h	Sol radiation MJMZ/day
Oct 23	0	3.6	30.0	17.5	95.0	59.0	6.6	5.7	16.0
24	0	3.0	29.6	19.6	96.0	53.0	3.0	6.0	13.3
25	0	5.0	30.5	17.5	93.0	39.0	4.9	9.8	17.1
26	0	4.2	29.5	17.3	94.0	45.0	4.8	7.8	14.7
27	0	5.4	29.5	15.0	92.0	35.0	5.9	11.0	20.6
28	0	5.6	29.6	14.8	92.0	27.0	5.4	11.0	21.1
29	0	4.8	29.6	15.5	90.0	35.0	4.2	11.0	20.5
30	0	4.8	30.4	17.4	94.0	40.0	4.8	10.7	19.9
31	0	4.3	30.5	18.0	87.0	37.0	4.3	10.3	18.1
Mean		4.5	29.9	16.9	92.6	41.1	4.9	9.3	17.9

Appendix N. Experiment 4: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations ($kgha^{-1}$) in an Alfisol in the micro-plots: following application of 50 kg urea N ha^{-1}.

	Time (h)					
	4	8	12	16	20	24
Surface soil 0-5 cm (a)						
Urea-N	-11.0	-21.9	-37.2	-39.9	-41.3	-42.6
NH_4^+-N	9.6	21.4	35.0	37.6	39.8	41.0
NO_2^--N	0	0	0.01	0.01	0	-0.01
NO_3^--N	-0.1	-0.2	-0.2	-0.2	0.8	0.8
Subsurface soil 5-10 cm (b)						
Urea-N	0	-1.2	-1.5	-1.6	-1.8	-2.2
NH_4^+-N	0.2	0.7	1.3	1.3	0.7	1.7
NO_2^--N	0	0	0	-0.01	0	-0.01
NO_3^--N	-0.2	-0.4	-0.2	-0.2	0.1	0
Total depth, 0-10 cm (a+b)						
Urea N hydrolysed (a+b)	11.0	23.1	38.7	41.5	43.1	44.8
Urea hydrolysis products recovered in 0-10 cm soil						
NH_4^+-N	9.8	22.1	36.3	38.9	40.5	42.7
NO_2^--N	0	0	0.01	0	0	0
NO_3^--N	-0.3	-0.6	-0.4	-0.4	0.7	0.8
Total	9.5	21.5	35.9	38.5	41.2	43.5
Nitrogen not recovered	1.5	1.6	2.8	3.0	1.9	1.3
As % of applied N	(14)	(7)	(7)	(7)	(4)	(3)

Appendix O. Experiment 4: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations (kg ha^{-1}) in an Alfisol in the micro-

	Time (h)					
	4	8	12	16	20	24
Surface soil 0-5 cm (a)						
Urea-N	-12.6	-47.2	-72.8	-81.8	-86.9	-89.3
NH_4^+-N	10.9	45.4	70.6	79.7	83.3	86.3
NO_2^--N	0	0.01	0.02	0.01	0.01	0
NO_3^--N	0	-0.1	-0.2	-0.3	0.5	1.4
Subsurface soil 5-10 cm (b)						
Urea-N	0	-1.6	-2.2	-2.5	-2.8	-3.3
NH_4^+-N	0.2	1.1	1.5	2.0	2.5	3.0
NO_2^--N	0	0	-0.01	-0.01	-0.01	-0.01
NO_3^--N	0	-0.4	-0.2	-0.2	-0.1	-0.01
Total depth, 0-10 cm (a+b)						
Urea N hydrolysed (a+b)	12.6	48.8	75.0	82.2	89.7	92.6
Urea hydrolysis products recovered in 0-10 cm soil						
NH_4^+-N	11.1	46.5	72.1	81.7	85.8	89.3
NO_2^--N	0	0.01	0.01	0	0	-0.01
NO_3^--N	0	-0.5	-0.4	-0.5	-0.6	1.3
Total	11.1	46.0	71.7	81.5	85.2	90.6
Nitrogen not recovered	1.5	2.8	3.3	0.7	4.5	2.0
As % of applied N	(12)	(6)	(4)	(1)	(5)	(2)

Appendix P. Experiment 4: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations (kg ha^{-1}) in a Vertisol in the microplots: following application of 50 kg urea N ha^{-1}.

	Time (h)					
	4	8	12	16	20	24
Surface soil 0-5 cm (a)						
Urea-N	-22.8	-29.3	-40.4	-42.2	-43.5	-45.6
NH_4^+-N	20.9	26.8	34.9	38.8	41.7	43.9
NO_2^--N	0.07	0.08	0.13	0.43	0.39	0.11
NO_3^--N	0.5	-0.7	-0.7	-0.3	-0.1	-1.2
Subsurface soil 5-10 cm (b)						
Urea-N	0	0	0	0	0	0
NH_4^+-N	0.4	0.1	-0.1	0.05	0.5	-0.1
NO_2^--N	0.01	0.01	0.02	0.02	0.02	0.02
NO_3^--N	0.5	0.5	0.1	-0.4	0.4	-0.1
Total depth, 0-10 cm (a+b)						
Urea N hydrolysed (a+b)	22.8	29.3	40.4	42.2	43.5	45.6
Urea hydrolysis products recovered in 0-10 cm soil						
NH_4^+-N	21.3	26.9	34.8	39.3	42.2	43.8
NO_2^--N	0.08	0.09	0.15	0.45	0.41	0.12
NO_3^--N	1.0	-0.2	-0.6	-0.7	0.3	-0.3
Total	22.4	26.8	34.6	39.1	42.9	43.6
Nitrogen not recovered	0.4	2.5	5.8	3.1	0.6	2.0
As % of applied N	(2)	(9)	(14)	(7)	(1)	(4)

Appendix Q. Experiment 4: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations (kg ha^{-1}) in a Vertisol in the micro-plots: following application of 100 kg urea N ha^{-1}.

	Time (h)					
	4	8	12	16	20	24
Surface soil 0-5 cm (a)						
Urea-N	-24.6	-65.5	-76.5	-81.8	-88.7	-93.0
NH_4^+-N	22.5	63.0	74.3	78.1	84.0	90.3
NO_2^--N	0.09	0.14	0.19	0.8	0.73	0.36
NO_3^--N	-0.7	-0.6	-0.2	-0.2	0.5	1.5
Subsurface soil 5-10 cm (b)						
Urea-N	0	0	0	0	0	0
NH_4^+-N	0.6	0.0	0.6	-0.1	0.6	0.2
NO_2^--N	0.02	0.02	0.03	0.04	0.04	0.05
NO_3^--N	-0.2	1.5	0	-0.6	-0.4	0.2
Total depth, 0-10 cm (a+b)						
Urea N hydrolysed (a+b)	24.6	65.5	76.5	81.8	88.7	93.0
Urea hydrolysis products recovered in 0-10 cm soil						
NH_4^+-N	23.1	63.9	74.9	78.0	84.6	90.5
NO_2^--N	0.11	0.16	0.22	0.84	0.77	0.41
NO_3^--N	-0.9	1.4	-0.2	-0.8	0.5	1.7
Total	22.3	65.5	74.9	78.0	85.9	92.6
Nitrogen not recovered	1.3	0	1.6	3.8	2.9	0.4
As % of applied N	(5)	(0)	(2)	(5)	(3)	(0)

Appendix R. Experiment 4: Weather data recorded at ICRISAT meteorology observatory during conduct of experiment 4, 27-28 February and 19-20 March 1988

Date	Rain mm	Evapo mm	Air temp (°C)		Rel humidity %		Wind Kh-1	Sunshine h	Sol radiation MJM2/day
			Max	Min	0717	1417			
					Alfisol Experiment				
27-2-88	0	7.4	35.8	22.0	92.0	21.0	10.8	10.7	20.6
28-2-88	0	7.4	35.5	21.5	96.0	22.0	11.6	10.2	19.6
Mean	0	7.4	35.6	21.8	94.0	21.5	11.2	10.5	20.1
					Vertisol Experiment				
19-3-88	0	9.4	36.8	20.2	45.0	17.0	8.9	11.0	22.7
20-3-88	0	9.5	35.5	18.5	41.0	20.0	6.0	10.9	22.4
Mean	0	9.5	36.2	19.4	43.0	18.5	7.5	11.0	22.6

Appendix S. Experiment 5: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations (mg N kg^{-1} soil) in soil samples from 0-5 cm depth of an Alfisol incubated: after addition of 66.6 mg urea-N kg^{-1} soil

	Time (h)					
	4	8	12	16	20	24
Urea-N	-10.2	-22.7	-53.1	-62.7	-64.6	-65.3
NH_4^--N	9.6	21.3	50.4	59.7	60.3	62.7
NO_2^--N	0	0.01	0.01	0.01	0	0
NO_3^--N	0.1	0.4	0.7	0.3	-0.1	-0.1
Total	9.7	21.7	51.1	60.0	60.2	62.6
Urea-N hydrolysed	10.2	22.7	53.1	62.7	64.6	65.3
Nitrogen not recovered	0.5	1.0	2.0	2.7	4.4	2.7
As % of applied N	(5)	(4)	(4)	(4)	(7)	(4)

Appendix T. Experiment 5: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations (mg N kg^{-1} soil) in soil samples from 0-5 cm depth of an Alfisol incubated after addition of 133.2 mg urea-N kg^{-1} soil.

	Time (h)					
	4	8	12	16	20	24
Urea-N	-13.1	-25.9	-110.6	-127.9	127.9	129.4
Urea hydrolysis products						
NH_4^--N	12.7	23.5	107.5	123.2	125.0	126.6
NO_2^--N	0.01	0.01	0.02	0.02	0.01	0.02
NO_3^--N	0	-0.2	0	0.1	-0.1	0.5
Urea-N hydrolysed	13.1	25.9	110.6	127.9	127.9	129.4
Nitrogen not recovered	0.4	2.6	3.1	4.1	3.0	2.3
As % of applied N	(3)	(10)	(3)	(3)	(2)	(2)

Appendix U. Experiment 5: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations (mg N kg^{-1}) in soil samples from 0-5 cm depth of a Vertisol incubated: after addition of 97 mg urea-N kg^{-1} soil

	Time (h)					
	4	8	12	16	20	24
Urea-N	-42.6	-67.2	-84.1	-96.2	-96.3	-96.3
Urea hydrolysis products						
NH_4^+-N	34.9	60.7	74.7	81.7	81.8	82.7
NO_2^--N	1.74	2.84	3.79	3.89	4.3	3.78
NO_3^--N	-1.2	0.2	1.1	1.8	-1.4	0.4
Total	35.4	63.7	79.6	87.4	84.7	86.9
Urea-N hydrolysed	42.6	67.2	84.1	96.2	96.3	96.3
Nitrogen not recovered	7.2	3.5	4.5	8.8	11.6	9.4
As % of applied N	(17)	(5)	(5)	(9)	(12)	(10)

Appendix V. Experiment 5: Net changes in urea, ammonium, nitrite and nitrate nitrogen concentrations (mg N kg^{-1} soil) in soil samples from 0-5 cm depth of a Vertisol incubated: after addition of 194 mg N kg^{-1} soil.

	Time (h)					
	4	8	12	16	20	24
Urea-N	-46.1	-71.1	-105.1	-159.8	-171.7	-189.3
NH_4^--N	39.9	65.2	93.4	149.3	160.3	177.5
NO_2^--N	1.48	2.72	3.69	6.76	7.3	6.28
NO_3^--N	0.5	1.3	0.9	2.3	-0.5	1.0
Total	41.9	69.2	98.0	158.4	167.1	184.8
Urea-N hydrolysed	46.1	71.1	105.1	159.8	171.7	189.3
Nitrogen not recovered	4.2	1.9	7.1	1.4	4.6	4.5
As % of applied N	(9)	(3)	(7)	(1)	(3)	(2)