EFFECTS OF SOIL WATER EVAPORATION AND POTENTIAL

ON UREA TRANSFORMATIONS IN SOIL

by

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cate this thesis to my father, Fernando Manuel Garcia.

CHAPTER 1

LITERATURE REVIEW

In recent years urea has become the world's leading N
fertilizer (Harre and Bridges, 1988). Urea accounted for
approximately 37% of the world nitrogen consumption in
1986 (FAO, 1987). In the USA, urea consumption has in-
creased more than any other product since 1968 with 15%
of the market in 1986 and 1987 (Harre and Bridges, 1988).
Reasons for the rapid rise in acceptance and the leading
importance of urea are its high analysis, its compatibil-
ity with other fertilizers, and its ease of storage and
handling.

Ammonia volatilization from surface-applied urea

Urea is used primarily as a dry, granular material or
as a solution of urea and ammonium nitrate (UAN). These
materials, when broadcast on the soil surface, are sub-
ject to N losses due to ammonia volatilization. Substan-
tial potential for NH_3 losses from surface-applied urea
and NH_4-N sources have been indicated by numerous inves-
tigators (Terman, 1979). If N fertilizers are incorporat-

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ed by tillage, NH_3 volatilization losses are typically very small.

Reduced tillage systems limit the opportunity to incorporate N fertilizers into the soil. Also topdress fertilization of small grain crops or permanent grass sods do not allow soil incorporation.

The volatilization process

The various reactions which govern NH_3 loss may be represented as

Adsorbed

$$NH_4^+ \rightleftharpoons NH_4^+(solution) \rightleftharpoons NH_3(solution)$$
$$NH_3(gas\ in\ soil)$$
$$NH_3$$

(gas in atmosphere)
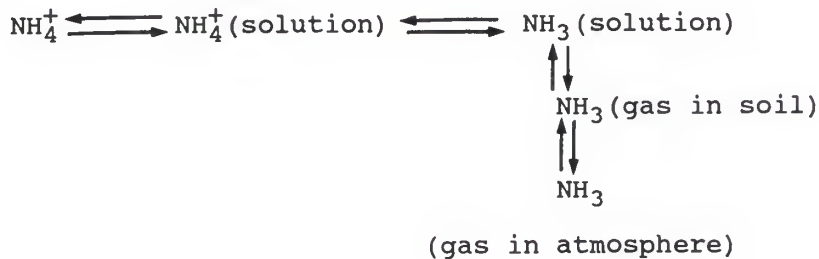
The rate of NH_3 volatilization may be controlled by the rate of removal and dispersion of NH_3 into the atmosphere, by changing the concentration of NH_4^+ or NH_3 in the soil solution, or by displacing any of the equilibria in some other way (Freney et al, 1983).

The driving force for NH_3 volatilization from a moist

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soil or a solution is normally considered to be the difference in NH_3 partial pressure between that in the liquid phase and that in the ambient atmosphere (Nelson, 1982). At equilibrium the amount of $NH_3(aq)$ is related to the NH_3 partial pressure in the atmosphere ($P\ NH_3$) by the Henry constant (K_H) according to

$$(P\ NH_3) = K_H\ [NH_3(aq)]$$

Because the NH_3 concentration in the air is low and relatively constant, the rate of ammonia volatilization from solutions is directly related to the $NH_3(aq)$ concentration.

Koelliker and Kissel (1988) defined the volatilization of NH_3 as a mass transfer of gaseous NH_3 from the soil solution to the air above the soil, driven by the difference in partial pressure of NH_3 between the soil solution and the air. They assume that the following simple mass-transfer equation applies for the process

$$d(NH_3)/dt = AK(P_1-P_g)$$

where

NH_3 = weight of NH_3 transferred, kg

t = time, hr

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A = area of soil solution-air interface, m^2

K = over-all mass transfer coefficient,
     kg hr^{-1} $(m^2)^{-1}$ atm^{-1}

P_1 = partial pressure of NH_3 gas in soil
     solution, atm

P_g = partial pressure of NH_3 in air above
     soil solution, atm

Vlek and Stumpe (1978) described the process of NH_3 loss from solution as a consecutive reaction with an opposite step

$$NH_4^+ \; \underset{k_3}{\overset{k_2}{\rightleftarrows}} \; NH_3(aq) + H^+ \; \overset{k_1}{\longrightarrow} \; NH_3(air)$$
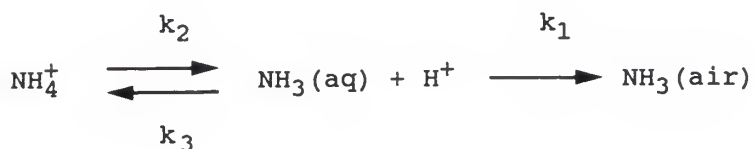
where the proportion of NH_4^+ and $NH_3(aq)$ depends on the initial pH, alkalinity, and buffering capacity of the system. This equilibrium between NH_4^+ and NH_3 in solution can be represented by

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$$\frac{[NH_3(aq)] \ [H^+]}{[NH_4^+]} \ = \ K \ = \ 10^{-9.5}$$

$$\log \frac{[NH_3(aq)]}{[NH_4^+]} \ = \ -9.5 + pH$$

At pH values of 5, 7 and 9 approximately 0.0036, 0.36 and 36 %, respectively, of the total ammoniacal N in the soil solution is presented as $NH_3(aq)$ (Nelson, 1982).

During the volatilization, the pH of unbuffered solutions decreases, because the H^+ formed as NH_4^+ is converted to $NH_3(aq)$. Vlek and Stumpe (1978) indicated that loss of NH_3 from a solution is accompanied by an equivalent loss of titratable alkalinity (HCO_3^-, CO_3^{2-}, OH^-) and the depletion of alkalinity to a sufficiently low pH practically terminates NH_3 volatilization.

Fenn and Kissel (1973) demonstrated that in calcareous soils ammonium salts that produced the highest loss of NH_3 were those that formed insoluble precipitates with Ca (F^-, SO_4^{2-}, HPO_4^{2-}) according to the following reactions

$$X \ (NH_4)_Z Y + N \ CaCO_3 \ (s) \rightleftharpoons N \ (NH_4)_2 CO_3 + Ca_n Y_x$$

$$(NH_4)_2 CO_3 + H_2O \rightleftharpoons 2 \ NH_3 + 2 \ H_2O + CO_2$$

$$2 \ NH_4OH$$
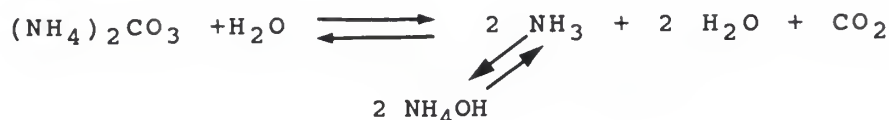
Feagley and Hossner (1978) suggested that NH_4HCO_3 is the intermediate formed when ammonium salts react with soil carbonates rather than $(NH_4)_2CO_3$ as reported by Fenn and Kissel (1973).

Predictive models are useful tools for evaluating the relative importance of various interdependent processes involved in a given system. In modeling the process of NH_3 volatilization, Koelliker and Kissel (1988) established as the most important chemical properties of a soil its titratable acidity and its cation exchange capacity. They also considered important the rate of NH_4^+ formation and fertilizer movement. In the model developed by R. Singh and Nye (1986), the amount of N lost from surface-applied urea is very sensitive to the initial pH of the soil, its pH buffer capacity, the rate of urea application and the soil urease activity.

Ammonia volatilization is affected by several factors

(Terman, 1979; Nelson, 1982; Hargrove, 1988). Among them, the source of ammonium used affects the potential of NH_3 losses. At the same time, the environmental conditions affect the reactions of the N fertilizer. Therefore, to understand the differences in NH_3 volatilization between sources, it is necessary to describe the transformations of the N fertilizer in the soil.

Urea transformations in soils

Dry granular urea must first undergo dissolution before it is subject to NH_3 volatilization. Granular dissolution of urea is mainly influenced by the soil water potential (Ferguson, 1985). If the soil water potential is low enough, urea will remain as a solid and will not be subject to NH_3 loss. If the soil contains enough water to start dissolving the granule, the soil solution immediately surrounding the granule becomes saturated with urea, resulting in urea diffusion outward from the granule. Urea hydrolysis can begin at this point (Volk, 1966).

Ammonia loss from urea is directly related to the hydrolysis rate (Kissel and Cabrera, 1988). Moe (1967) and Bremner and Douglas (1971) found reduced losses when urease activity was inhibited. A slower rate of urea

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hydrolysis was suggested as the main factor of the decline in NH_3 losses by several authors (Ernst and Massey, 1960; Craig and Wollum, 1982; Black et al, 1985; McInnes et al, 1986a).

As urea must be dissolved and contact the urease enzyme for hydrolysis, surface applications may be less subject to initial loss of NH_3 than are NH_4-N sources (Terman, 1979). Overrein and Moe (1967) found that the rates of urea hydrolysis and NH_3 volatilization were directly related to the rate of urea application. Reynolds and Wolf (1987a) related NH_3 volatilization to NH_3 production from urea hydrolysis in seven soils with a broad range of urease activity levels. They found that although reducing the urease activity in a given soil might be expected to reduce NH_3 volatilization, NH_3 volatilization losses would not be predicted from urease activity alone without consideration of other properties. They suggested, from the results of the study, that a low hydrogen ion buffering capacity was a better indicator of the potential for NH_3 volatilization from surface-applied urea than soil pH or urease activity.

Urea hydrolysis rates slow considerably and approach zero when surface soil becomes very dry (Ferguson and Kissel, 1986; McInnes et al, 1986a; Reynolds and Wolf,

1987b). Urea hydrolysis seemed to be more related with water potential than with gravimetric water content (Kissel and Cabrera, 1988). Urease activity was maximum at about -0.02 MPa soil water potential, decreasing as the soils approach saturation. The decrease in urease activity was more substantial at water potentials less than -0.02 MPa. More information is needed to develop an appropriate curve to relate the urease activity and the soil water potential.

Delaune and Patrick (1970) reported about the same urea hydrolysis rate in water-logged soils and in soils kept at -0.033 MPa moisture. Vlek and Carter (1983) showed that the rate of urea hydrolysis in four soils declined slightly with decreasing water contents, but did not drop significantly until the permanent wilting point of the soil was reached.

Effect of soil water content on ammonia volatilization

Studies on the effect of initial soil water content on NH_3 volatilization showed generally that NH_3 losses increase with increasing soil moisture content up to field capacity (Ernst and Massey, 1960; Volk, 1966; Fenn and Miyamoto, 1979; Black et al, 1985; Bouwmeester et al,

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1985).

In studies where drying of soil was minimal, some workers found that NH_3 losses decrease with increasing initial soil moisture content (Overrein and Moe, 1967; Fenn and Escarzaga, 1976; Prasad, 1976; O'Toole and Morgan, 1988).

Ernst and Massey (1960) found a direct relationship between NH_3 volatilization and initial soil moisture content under laboratory conditions. Differences in NH_3 losses from soils at moisture contents ranging from 5 % to 37.5 % were significant at the 1 % level, with the higher moisture contents showing the greater percentage of NH_3 losses. Volk (1966) suggested that rapid losses of NH_3 from moist surfaces were due primarily to faster hydrolysis rates at the higher water contents.

Overrein and Moe (1967) evaluated the effect of two different soil moisture contents (10 and 20 %), in combination with different depths of urea application on NH_3 volatilization loss under laboratory conditions. They observed significantly greater losses at the low soil moisture content at each depth of urea application. They attributed these differences between the two levels of soil moisture to the high solubility of NH_3 in water.

Prasad (1976) conducted laboratory experiments to

compare the volatilization of NH_3 in a calcareous soil from sulfur-coated urea, ammonium sulfate, and urea, each at two temperatures (22 and 32° C) and three soil moisture levels (25, 50 and 80 % of the water holding capacity). At both temperatures increasing soil moisture levels led to a reduction of NH_3 loss regardless of the N-source.

Fenn and Escarzaga (1976) evaluated the influence of soil water content, type of N compound and nitrogen application methods on NH_3-N losses from highly calcareous soils. They found that NH_3 losses from ammonium sulfate were greater at 13 to 30 % soil water than at 55 % soil water. With 0 and 8 % soil water, little NH_3 was lost because no dissolution occurred. Urea and urea-$NH_4H_2PO_4$ mixtures resulted in low total NH_3- losses. In dry soils urease activity was inhibited resulting in low total N losses. The same authors in other paper (Fenn and Escarzaga, 1977), reported the results of a series of studies designated to evaluate the effect of the initial soil water content and water additions on NH_3 loss. Initially wet soil resulted in higher NH_3 loss from ammonium nitrate and ammonium sulfate than from initially dry soil in most cases. Addition of increasing water following surface application of N quantities reduced

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total NH_3 loss, but did not eliminate differences between the different initial soil water contents.

Volatilization loss of NH_3 from surface-applied urea was slightly greater under -0.033 MPa moisture conditions than under water-logged conditions (Delaune and Patrick, 1970). From these results the authors concluded that NH_3 volatilization will be lower in water-logged rice fields than in unflooded fields. Shimpi and Savant (1975) found that increasing the moisture content from 30 to 100 % resulted in increased NH_3 retention in noncalcareous and lateritic soils. Continuous submergence favored NH_3 retention in both soils.

Water additions to the soil following surface fertilizer applications can have a significant effect on the potential for NH_3 volatilization. Fenn and Miyamoto (1979) studied the behavior of urea in a calcareous soil under the influence of different amounts of water added and initial soil water content. Ammonia loss from surface-applied urea to an initially moist soil was decreased with increasing water additions. Ammonia losses were significantly less from initially dry soils than from initially wet soils at all levels of water additions. They found that urea moved largely with the wetting front and concluded that even if the soil is ini-

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tially wet or dry, the potential for NH_3 loss from urea is rapidly lowered with increasing quantities of water applied.

Craig and Wollum (1982) evaluated the effect of precipitation and season of fertilizer application on the gaseous losses of NH_3 and the chemical changes in the soil from applications of urea and ammonium nitrate (AN). Considerably more gaseous NH_3 was lost from urea than from AN. Ammonia volatilization from urea appeared to be dependent on soil moisture and time and amount of precipitation after fertilizer application. During periods of high temperature and low precipitation but with adequate moisture for urea hydrolysis, loss of NH_3 would be greater than during periods of low temperatures and large amount of precipitation. Rainfalls of 5 mm provided adequate soil moisture for hydrolysis and subsequent NH_3 losses. Rainfalls of 30 mm or more leached the urea or ammoniacal-N deeper into the soil decreasing NH_3 losses.

Harper et al (1983) measured soil and microclimate factors to determine their influence on aerial NH_3 transport before and after fertilization periods. Immediately after urea application the NH_3 efflux increased to high rates when the soil was wet. If the soil surface was dry the NH_3 efflux increased slowly to moderate levels, maybe

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as a result of incomplete urea hydrolysis. Rainfall of about 5 mm or more substantially reduced NH_3 efflux and the duration of the efflux period. The authors suggested that the amount and distribution of rain after urea application controlled the total NH_3 losses. The rain reduced NH_3 efflux by dispersing the urea in the soil and thus limiting the development of high concentrations of NH_4^+-N and NH_3 near the soil surface.

In greenhouse experiments using ^{15}N, Bouwmeester et al (1985) found that the amount of N loss was affected to some extent by initial soil moisture content, but particularly by rainfall. A 4 cm rainfall seven days after urea addition decreased N losses by approximately 30 % regardless of the initial soil moisture content. In wind tunnel experiments, the same authors found that a 2.5 cm rainfall immediately after urea application was sufficient to avoid N losses.

McInnes et al (1986a) used a mass-balance micrometereological method, which produces very minimal disturbance of the natural environment, to evaluate the magnitude of NH_3 volatilization and how some environmental factors affected the rate of loss under field conditions. Results from their studies suggest that soil water content and temperature have a strong influence on NH_3 losses from

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surface-applied urea. They stated that NH_3 losses fol-
lowed most closely the pattern of urea hydrolysis. Urea
hydrolysis approached zero when the soil surface was near
"air dryness". Rainfall of 0.86 cm or irrigation of 0.5
cm seven days after fertilizer application did not pre-
vent further N loss, but rather enhanced the rate of
volatilization.

The same authors in another study (McInnes et al,
1986b), assessed the loss of NH_3 and observed the associ-
ated N transformations and movement in the field follow-
ing broadcast application of UAN solution to soil with
wheat straw at the soil surface. They used the same
mass-balance micrometereological method as in the previ-
ous study. Results obtained in these experiments agreed
with those obtained applying urea to a bare soil. Volati-
lization losses followed the pattern of urea hydrolysis
with both processes being quite sensitive to the avail-
ability of water. Simulated rainfalls of 2.5 mm increased
NH_3 losses, but rainfalls of near 30 mm moved much of the
fertilizer below the 40-mm soil depth reducing NH_3 loss-
es.

The effect of soil water content on urea hydrolysis
and subsequently on NH_3 volatilization, was also observed
by Ferguson and Kissel (1986). In laboratory experiments

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they observed that rapid drying of the soil quickly decreased the rate of NH_3 loss and the amount of urea that hydrolyzed. They concluded that the potential for NH_3 volatilization from surface-applied urea in an initially moist soil that dries rapidly is low if the soil water content/potential falls to a level at which urea hydrolysis is inhibited.

Keller and Mengel (1986) in field experiments measuring NH_3 loss from fertilizers applied to corn residue found that 25 mm of rain 50 hours after application ended NH_3 volatilization.

Black et al (1987) examined the effect of time of water application, relative to the time of urea application, on the magnitude of volatile loss of NH_3 from soils of varying initial soil moisture status. They found that when urea was surface-applied on an air dry soil, NH_3 volatilization rates were low but extended over a long period. The rate of NH_3 loss increased immediately after application of water but the total loss was minimized from air dry soil when sufficient water was applied (> 16 mm). When initial soil moisture conditions were favorable for rapid urea hydrolysis, water additions within hours of spreading urea reduced NH_3 loss.

McGarry et al (1987) in Ireland found that maximum

loss rates of NH_3 following urea applications were responsive to temperature and, less markedly, to soil moisture content. Loss in the wet samples (85% field capacity) were much less temperature-dependent than in the dry samples (35% field capacity). Under minimal drying conditions, NH_3 volatilization was greater in the dry treatment than in the wet one. Simulated rainfall reduced NH_3 volatilization, although its effectiveness varied in different soils.

The effect of soil water content on NH_3 loss from surface-applied urea is clearly influenced by the effect of soil water on the rate of urea hydrolysis. As noted in the works cited above, optimum conditions for urea hydrolysis generally induced high rates of NH_3 volatilization. High soil moisture contents and subsequent slow to moderate rates of drying resulted in greater NH_3 loss than from urea applied to dry soils or soils under conditions of rapid drying.

Effect of soil water evaporation on ammonia volatilization

Since upward movement of water helps transport NH_3 to the soil surface, a relationship between NH_3 and water

loss from soils might be expected. A number of research-
ers have reported a direct relationship in laboratory
studies between NH_3 and water loss (Jewitt, 1942; Martin
and Chapman, 1951; Wahhab et al, 1957; Fenn and Escarza-
ga, 1977).

Jewitt (1942) reported that the initial soil moisture
content did not greatly affect NH_3 volatilization from
ammonium sulfate-treated alkaline soil, but the amount of
NH_3 loss was related to the amount of water loss. Martin
and Chapman (1951) observed no volatilization of NH_3 when
moist air was passed over N-fertilized soil samples, but
loss of NH_3 occurred when the samples were aireated with
dry air and then were losing moisture. In determining the
effect of soil moisture and depth of application on
retention of anhydrous ammonia, Stanley and Smith (1956)
observed upward movement of NH_3 in soils with 15-23%
moisture. As water evaporated from the surface, NH_3 moved
to the surface and volatilized to the atmosphere. Wahhab
et al (1957) found that NH_3 loss was not entirely inde-
pendent of the original soil moisture content and that
there was a constant ratio between NH_3 and moisture
losses when ammonium sulfate was applied to alkaline
soils of Pakistan.

However, Ernst and Massey (1960) stated that the loss

of NH_3 by volatilization was not related to the rate of drying of the soil. They found that NH_3 loss from surface-applied urea was nearly the same regardless of the amount of water lost. Chao and Kroontje (1964) studied the relationship between water loss and NH_3 volatilization. The rate of NH_3 loss decreased with time, while the rate of water evaporation stayed constant until the soil was nearly air-dry.

Fenn and Kissel (1976) suggested that water loss influenced NH_3 loss from NH_4-compounds applied at different soil depths. A direct relationship was found by Fenn and Escarzaga (1977), between the loss of water and loss of NH_3 from sand. Data indicated that the rate of loss of NH_3 decreased faster than the rate of loss of water. They also observed that interrupting the capillary continuity of the sand decreased the amount of NH_3 and water loss, but did not alter the ratio of NH_3 to water losses in the long term.

The speed with which air flows across the soil and the relative humidity of the air can have a significant effect on both water and NH_3 loss. A certain air velocity is necessary in order to reach the point where the partial pressure of the NH_3 in the atmosphere is not inhibiting NH_3 volatilization from the soil solution (Kissel

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et al, 1977). Water evaporation from the soil is con-
trolled in part by the partial pressure of water in the
atmosphere (relative humidity) and wind speed.

Denmead et al (1982) measured NH_3 volatilization from
NH_3 injected into flood irrigation water applied to corn.
The NH_3 equilibrium vapor pressure and wind speed both
affected loss. Ammonia loss increased with the approxi-
mate square of the wind speed.

However, work by Hargrove et al (1977) showed that the
highest NH_3 loss rates from ammonium sulfate applied to a
bermuda grass sod, occurred at the highest relative
humidities of the air. They attributed this relationship
to factors related with the dissolution of the fertilizer
granule, the reaction of AS in the soil, and the competi-
tion of NH_3 and water vapor for sorption sites.

Bouwmeester et al (1985) conducted wind tunnel experi-
ments to determine the effect of environmental factors on
NH_3 loss from urea applied to the soil surface. They
found that dry soil conditions created by high wind
speeds decreased NH_3 volatilization due to a lack of
moisture in the soil surface. They stated that the wind
speeds they used were 10 to 100 times greater than those
used by other researchers in laboratory studies and that
their conditions were more representative of soil drying

conditions in the field. When soil was moist, increasing wind speed increased NH_3 volatilization.

Harper et al (1983) measured NH_3 loss from urea applied to a subtropical pasture. They found that during the summer the soil surface temperature was the most highly correlated factor influencing NH_3 flux density but that during the remainder of the year, the evapotranspiration rate was most highly correlated with NH_3 loss.

McInnes et al (1986a) suggested that capillary movement of water to the evaporating surface increased the concentration of NH_3 and thus the NH_3 loss after a rain of 0.86 cm. In other experiments, the same authors (McInnes et al, 1986b) found that the major peaks of NH_3 loss from UAN solution applied to straw residue occurred at noon when the wind speed was relatively high, the straw temperature was near its maximum, and the straw-water content was decreasing.

Ferguson and Kissel (1986) evaluated the effects of rapid water evaporation from the soil on the movement of urea and its hydrolysis products. They found that urea can be transported via mass flow to the soil surface in the evaporating water stream even after diffusing to substantial depths. When the soil water content/potential was not adequate to support urea hydrolysis, the urea at

the soil surface was not susceptible to N loss by volatilization.

Kucey (1988) working with calcareous soils in Canada, also observed that NH_3 volatilization increased as a soil dried until the soil moisture dropped below a level that greatly slowed or stopped urea hydrolysis.

Reynolds and Wolf (1987b) studied the effect of soil moisture and air relative humidity on NH_3 loss from surface-applied urea. Air flows of different relative humidity contents created different evaporative demands. The initial soil water potentials evaluated were -0.033 MPa with and without water replenishment, and < -1.5 Mpa without water replenishment. Greater NH_3 losses were observed in treatments where the supply of water to the soil surface was not limiting and evaporation was proceeding at a constant rate. Rapid drying of the soil resulted in low NH_3 loss as in the work of Ferguson and Kissel cited above. At a high initial soil water potential the influence of the air relative humidity in the 25 to 85 % range was negligible, but at the low initial soil water potential a high air relative humidity facilitated NH_3 loss from urea.

From the results obtained by the different authors, we might conclude that loss of water from soil promotes NH_3

evolution by increasing the $NH_3(aq)$ in solution at the soil surface , and thereby increasing NH_3 volatilization. However, despite the large volume of literature on the subject, none of the work clearly shows the effect of water evaporation on concentrating NH_3 (aq) near the soil surface.

Urea hydrolysis in soils

Under optimum conditions urea applied to the soil is rapidly hydrolyzed to NH_4^+ and HCO_3^- ions. This reaction is hydrolyzed by the enzyme urease

$$CO(NH_2)_2 + 2H_2O + H^+ \;\; \xrightleftharpoons[\text{urease}]{} \;\; 2NH_4^+ + HCO_3^-$$

In general, most workers indicated that soil urease is largely of microbial origin, but still its origin is not well known (Bremner and Mulvaney, 1978). It is believed that urease is a free microbial extracellular enzyme that may be complexed to soil organic constituents, thereby being inaccessible to destruction by proteinases (Ladd, 1978; Bremner and Mulvaney, 1978). Paulson and Kurtz (1969) considered soil urease in two components: microbi-

al urease, associated with soil microorganisms, and adsorbed urease, adsorbed by soil colloids.

Urea hydrolysis may be described by first order kinetics when it is heterogeneously applied to the soil surface (Vlek and Carter, 1983: Kumar and Wagenet, 1984; and Yadav et al, 1987). When urea is mixed uniformly with the soil, hydrolysis fits zero-order kinetics (Vlek and Carter, 1983).

Kissel and Cabrera (1988) discussed the major effects that control the rate of urea hydrolysis. They distinguished two processes: i) the movement of urea towards the urease enzyme, and ii) the actual hydrolysis reaction itself. The first process resulted from molecular diffusion or movement with mass flow of water. The second process, reaction of urea with urease, depends on the number of active urease molecules and the factors that affect their activity.

The number of active urease molecules in soil cannot be measured directly but it can be estimated as the soil's urease activity under standard conditions of temperature, pH, and available water (Kissel and Cabrera, 1988). Urease activity was correlated with soil properties by several authors. The best correlations were obtained with soil organic carbon and total nitrogen

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(Gould et al, 1973; Zantua et al, 1977; Reynolds et al, 1985; O'Toole and Morgan, 1988).

Four major factors affect urease activity: urea concentration, soil pH, soil temperature, and soil water. Bremner and Mulvaney (1978), Gould et al (1986), and Kissel and Cabrera (1988) have reviewed research on the factors affecting urease activity.

Effect of soil water on urease activity in soils

Different results for the effect of soil water content on the rate of urea hydrolysis have been found, possibly due to differences in experimental conditions.

Overrein (1963) found that the soil moisture content had no statistically significant effect on the hydrolysis of urea in soil. He worked with a Chalmers silty clay loam soil with moisture contents of 10 and 22%. Simpson and Melsted (1963) working with six different soils of Illinois, found that soil moisture had a relatively small influence on urea hydrolysis rates compared to the effect of pH and temperature. In general rates of hydrolysis were slightly lower at 60% moisture content than at 24%.

Delaune and Patrick (1970) reported no differences in the rate of urea hydrolysis at 0.033 MPa moisture and

under waterlogged conditions for eleven Alluvial and Coastal Prairie soils in Louisiana.

In Alberta soils, Gould et al (1973) observed small effects of soil moisture on urea hydrolysis and concluded that soil water content was not an important factor affecting urea hydrolysis. They conducted the experiment with moisture contents between 24 and 100%.

Dalal (1975) investigated the effect of urea concentration, soil water content, period of storage, temperature and toluene on urease activity of 15 Trinidad soils. He found that urease activity increased from 25 to 50% of water holding capacity (WHC). Above 50% WHC, the activity decreased slightly for some soils and considerably for others. Similar results were obtained by Sankhayan and Shukla (1976) in India. They studied the effect of two levels of soil moisture on the rate of urea hydrolysis in five soils and observed that the rate was faster at 40% WHC than at 60% WHC. They attributed these results to the lower availability of O_2 in the 60% WHC treatment.

Vlek and Carter (1983) observed a drastic reduction in urease activity at water contents less than the permanent wilting point. At these low moisture levels, the lack of

free water in the soil may prevent diffusion of applied

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urea (Sadeghi et al, 1989), thus limiting the contact between urea and soil urease. At higher water contents urea hydrolysis rates were less dependent on soil moisture content. Campbell et al (1984) also found a greater rate of hydrolysis at -0.03 MPa than at -1.5MPa in three Australian soils.

Kumar and Wagenet (1984) investigated the effect of four soil moisture contents (25, 50, and 100% of field capacity and flooding), on urea hydrolysis in three soils of Utah and California. They found that urease activity increased from 25% of field capacity to 100%, but it decreased when the soil was flooded.

In vertisol and alfisol soils of India, Sahrawat (1984) found no urease activity under air-dry conditions that were far below -1.5 MPa. As soil water content increased from air-dry to field capacity, urease activity increased in both soils. Any increase of soil water content over field capacity did not modify urease activity. Yadav et al (1987) in clay and sandy loam soils of India also found that the rate of urea hydrolysis increased from 20 to 100% of field capacity. In their study they observed that flooding decreased the rate of hydrolysis.

Yadvinder-Singh and Beauchamp (1988) investigated the

effect of soil water potential on urea transformations in two Canadian soils. They found that the rate of urea hydrolysis decreased as soil water potential decreased from -0.035 MPa to -0.120 MPa.

O'Toole et al (1985) also observed that the rate of hydrolysis increased from permanent wilting point to field capacity.

In summary, urea hydrolysis rate increases as soil water content increases above air-dry. In the range between permanent wilting point and field capacity it can increase slightly or remain constant. Finally, urease activity decreases or remains constant as the soils become saturated . Kissel and Cabrera (1988), in reviewing the effect of soil water content on urea hydrolysis, concluded that a better relationship can be found with soil water potential than with gravimetric water content. They also emphasized the lack of data for the very low water contents that routinely occur at the soil surface under dry conditions.

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Chapter 2

Effect of soil water evaporation on ammonia
volatilization from surface-applied urea

Surface-applied urea is susceptible to losses of ammo-
nia by volatilization when applied to soil. The magnitude
of the loss is affected by soil, environmental, and man-
agement factors. Soil properties determine the potential
of ammonia volatilization, but the actual magnitude of
loss in the field is determined by environmental factors
(Hargrove, 1988). Soil temperature, soil water content-
potential, soil water flux and wind speed are considered
the most important environmental factors (McInnes et al,
1986a).

Earlier work by Jewitt(1942), Martin and Chapman
(1951), and Wahhab et al (1957) indicated that the rate of
soil water movement and ammonia losses were correlated.
However Ernst and Massey (1960), Chao and Kroontje (1964)
and Terman et al (1968) demonstrated that the rates of
ammonia and water loss were not related.

More recent studies indicate that greater volatiliza-
tion of ammonia occurs when soil moisture is lost (Fenn
and Escarzaga, 1977; Harper et al, 1983; McInnes et al,

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1986a). Rapid evaporation of soil water may increase the concentration of NH_4^+-N and NH_3-N in solution at the soil's surface, thereby increasing the partial pressure of ammonia and the potential for volatilization.

Despite the work done previously, the effect of water loss on NH_3 volatilization has not been quantified. The objectives of this research were to evaluate the effect of different evaporation rates on i) NH_3 volatilization, and ii) the movement of urea and its hydrolysis products.

Materials and Methods

Research was conducted through laboratory experiments.

We modified a laboratory apparatus previously designed by Ferguson and Kissel (1986) (Figure 1). Using this apparatus, different evaporation rates were created by passing air of different relative humidities over soil packed into a plexiglass chamber. The relative humidity of air was controlled by bubbling air into sulfuric acid at different concentrations. After the air stream left the sulfuric acid pretrap, a thermocouple psychrometer connected to a multimeter measured the relative humidity of the air. The air was then passed over the soil surface and bubbled into 0.05 M H_2SO_4 solution to trap the NH_3 evolved

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and into 2 M KOH solution to trap the CO_2. Finally the air stream was passed through a dessicator and a flowmeter where the airflow was regulated.

Soil was packed into the plexiglass cylinder chambers to a bulk density of approximately 1.4 Mg m^{-3} and a depth of 45-50 mm on top of a 0.5 bar ceramic plate. The ceramic plate was the top part of an acrylic piston that allowed the soil to be pushed out the top of the cylinder for sampling at the end of the experiment. Water inside the piston was connected to a water reservoir via nylon tubing. The water reservoir was connected to a vacuum pump that allowed control of the water potential in the reservoir and the soil in the chamber. The objective was to maintain a constant soil water potential in both treatments during the experiment.

The soil used in the experiments was collected from an area mapped as Captina silt loam (fine silty, mixed, mesic Typic Fragiudults) at the Agronomy Farm of the University of Arkansas. The soil was passed through a 2 mm sieve, mixed and placed in a container. The container was tightly sealed and stored at room temperature. Previous to the experiment, the soil was leached with a N-free nutrient solution to decrease the level of NO_3^--N and NH_4^+-N. The N-free nutrient solution contained 100 mg Ca/L, 24 mg

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Mg/L, 113 mg S/L, 0.5 mg P/L, and 4 mg K/L prepared with KH_2PO_4, K_2SO_4, $MgSO_4$, and $CaSO_4$. The final pH was approximately 7 (Cabrera and Kissel, 1988). After leaching, the soil was passed through a 2 mm sieve again.

Two different relative humidities of air were set up. Air at 75 % relative humidity was produced by bubbling into 4.5M H_2SO_4. Air at 95 % relative humidity was produced by bubbling into 1M H_2SO_4. Air at 75 % relative humidity was called dry air treatment or high evaporative rate treatment, air at 95 % was called wet air treatment or low evaporative rate treatment. The airflow rate was maintained constant for both treatments at 13 chamber volumes min^{-1} (1.2 L min^{-1}).

After packing the soils into the plexiglass chambers, the system was allowed to equilibrate. After 24 hours, urea was applied uniformly as finely ground crystals to the soil surface of two chambers, one of the dry air treatment and the other of the wet air treatment. The rate of urea used was equivalent to 200 kg N ha^{-1}. For each treatment, a control chamber without application of urea was established.

The solutions of the 0.05 M H_2SO_4 traps were changed at 12 hours intervals to measure NH_3-N evolved from the soil. The solutions were diluted to 25 mL with 0.05 M H_2SO_4

solution and analyzed for NH_4^+-N with a Technicon Autoanalyzer II system (Technicon Industrial Systems, 1977b).

The CO_2 from microbial respiration in the soil dominated the amounts of CO_2 evolved. Total CO_2 measured at the end of the 12 hour-interval periods ranged from 300 to 400% of the applied urea-C, and the differences between fertilized and control treatments were small. For these reasons, the values of CO_2 evolved are not presented.

At the end of the experiment, the soil in the chambers was sampled at 0-2, 2-5, 5-10, 10-15, 15-20, 20-30, 30-40, and 40-50 mm depth by pushing it out of the top of the chamber with the piston. Each layer was transferred to a tared Erlenmeyer flask. A subsample of the soil from each layer was taken for gravimetric soil water content determination. After each soil layer was weighed, enough water was added to make a 1:1 paste and pH was measured. Soil pH values were measured with a combination microelectrode and an Orion 701A pH meter. After pH measurement, 50 mL of 3.2 M KCl-8 mg kg^{-1} PMA (phenylmercuric acetate) solution was added to the flask and the flask shaken for 30 minutes. The soil suspension was then transferred to a Buchner funnel under suction, filtered through Whatman # 41 filter paper, and leached 3 times with 15 mL of 2 M KCl-PMA solution. The leachate was diluted to 200 mL with 2 M

KCl-PMA solution and frozen until analysis could be performed. The leachate was analyzed colorimetrically for urea using the procedure of Douglas and Bremner (1970), and for ammonium and nitrate using Technicon Industrial Systems procedures (1977a and 1977b). All analysis were performed on a Technicon Autoanalyzer II system.

Evaporation was calculated from the consumption of water in the water reservoir and the difference between the wet and the dry weight of the soil at the beginning and the end of the experiment. Calculation is as follows

$$E = WC - ((WWE - DWE) - (WWB - DWB))$$

where

E = evaporation, mL

WC = water consumption from the reservoir, mL

WWE = wet weight of the soil at the end, g

DWE = dry weight of the soil at the end, g

WWB = wet weight of the soil at the beginning, g

DWB = dry weight of the soil at the beginning, g

The experiment was run four times with each considered a replication. It was analyzed as a Randomized Complete Block Design, with the relative humidity of the air stream as treatments and replications as blocks. Values of NH_3 loss are reported after subtracting volatilization from unfertilized control chambers. The amount of NH_3 loss from

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unfertilized soil was very small.

Calibration of thermocouple psychrometer

The temperatures of the wet and dry bulbs of the thermocouple psychrometer were calibrated with the multimeter output by using a water bath at different temperatures. An equation was fitted for each bulb using a SAS nonlinear procedure (SAS Institute Inc., 1985).

Wet bulb

$$\text{Temperature} = 58.97 * e^{(-0.00864 * output)}$$

$$R^2 = 0.994$$

Dry bulb

$$\text{Temperature} = 59.32 * e^{(-0.00878 * output)}$$

$$R^2 = 0.995$$

where the temperature was in $^{\circ}$C, and the output in microvolts. The relative humidity was obtained from tables given by Unwin (1980), with the value of the dry bulb temperature and the wet bulb depression.

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Results and Discussion

The amount of ammonia-N volatilized, expressed as
cumulative percentage of the urea-N applied and as per-
centage of the urea-N hydrolyzed, and water evaporation
for the dry air and the wet air treatment in each replica-
tion are given in Table 1. The percentages of urea-N
hydrolyzed, urea-N nitrified, and urea-N accounted for at
the end of each replication are presented in Table 2. The
urea-N hydrolyzed was calculated in two different ways: i)
by appearance of ammonium-N, nitrate-N, and ammonia-N
after subtracting the values observed in the control
chambers, and ii) by accounting for disappearance of urea.
The soil water content, pH, NH_4^+-N, NO_3^--N, and urea-N in
the soil at the end of each replication is presented in
Tables 3 to 6 and Figures 3 to 7.

In spite of the large differences in soil water evapo-
ration between treatments, no significant differences in
NH_3 volatilization between the wet air and the dry air
treatments were found (Tables 1 and 7). Ammonia volatili-
zation as a percentage of urea-N added in the dry air
treatment was higher than in the wet air treatment in
replications 1 and 2, but in replications 3 and 4 there
were no differences between treatments (Table 1, Figure
2). Differences between treatments in replications 1 and 2

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are much higher if we compare the values of NH_3 volatilization as a percentage of urea-N hydrolyzed (Table 1). In replications 3 and 4, differences in volatilization were small expressed as a percentage of urea-N hydrolyzed.

Hargrove (1988) divided the factors affecting NH_3 volatilization into three categories : soil, environmental, and management factors. Under well controlled laboratory conditions we could maintain these factors constant, however, in our experiment soil water content varied between replications and treatments (Tables 3, 4, 5, and 6). Soil water content can affect urea hydrolysis (McInnes et al, 1986a), but this effect may possibly be eliminated if we express volatilization as a percentage of urea-N hydrolyzed. In replications 1 and 2 (Tables 3 and 4, and Figure 3), the soil water content in the wet air treatment was higher than in the dry treatment and urea hydrolysis was higher in the wet treatment. More urea hydrolysis was probably caused by deeper diffusion in the wet treatment (Figure 7), allowing the urea to contact more urease enzyme. In both replications 1 and 2, there were differences in volatilization. In replications 3 and 4 (Tables 5 and 6, and Figure 3), there were no differences in soil water content between treatments but urea hydrolysis and ammonia volatilization were almost the same in both treatments. Reynolds and Wolf (1987b) found that ammonia volat-

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ilization was higher under drying than under water replenishment conditions. They attributed these results to a faster urea hydrolysis in the drier soil, or a greater ammoniacal-N concentration at the soil surface in the drier soil, or a combination of the two effects. In our study, urea hydrolysis was significantly faster in the wet treatment than in the dry treatment. In greenhouse pot experiments, Terman et al (1968) reported similar losses of ammonia from surface-applied urea at 70 and 100% air relative humidity in a Hartsells fine sandy loam. Chao and Kroontje (1964) found similar cumulative losses of NH_3 for water saturated air and dry air. The water saturated air did not dry the soil, but the dry air produced much dryer soil by the end of the experiment.

We should also consider that ammonia diffusion in air is more rapid than in solution. Therefore, volatilization may be reduced in wet soils in the range of soil moisture of our study (Freney et al, 1983; Sadeghi et al, 1988). Soil water content in replications 3 and 4 was higher than in replications 1 and 2, but had lower volatilization than replications 1 and 2 in both treatments. It is also interesting to notice that in replications 3 and 4 the level of volatilization was very low when compared to other experiments done under laboratory conditions (Hargrove and Kissel, 1979; Terman, 1979).

In order to compare ammonia volatilization in both treatments by replication, we tested if the model describing cumulative NH_3 loss over time was the same for both treatments. The null hypothesis to test was that one model can describe cumulative volatilization for both treatments. Then, fitting a model to data from the wet and dry treatments, we estimated the residual sum of squares for the null hypothesis. The alternative hypothesis was that one model cannot describe cumulative volatilization for both treatments, i.e. each treatment should be described by a separate model. The residual sum of squares for the alternative hypothesis was calculated by adding the residual sum of squares of the two separate models. The difference between the residual sum of squares of the null and the alternative hypothesis gave an estimation of the residual sum of squares due to deviations from the null hypothesis. The models used were

Ho, null hypothesis:

First Replication	Loss = $e^{0.0141T}$	R^2 = 0.763
Second Replication	Loss = $e^{0.01T}$	R^2 = 0.827
Third Replication	Loss = $e^{0.00876T}$	R^2 = 0.874
Fourth Replication	Loss = $e^{0.0096T}$	R^2 = 0.927

Ha, alternative hypothesis:

First Replication

Dry treatment	Loss = $e^{0.0159T}$	R^2 = 0.955

Wet treatment   Loss = $e^{0.0115T}$ $R^2 = 0.873$

Second Replication

    Dry treatment   Loss = $e^{0.011T}$ $R^2 = 0.938$

    Wet treatment   Loss = $e^{0.00875T}$ $R^2 = 0.841$

Third Replication

    Dry treatment   Loss = $e^{0.00897T}$ $R^2 = 0.894$

    Wet treatment   Loss = $e^{0.00852T}$ $R^2 = 0.859$

Fourth Replication

    Dry treatment   Loss = $e^{0.00968T}$ $R^2 = 0.923$

    Wet treatment   Loss = $e^{0.00953T}$ $R^2 = 0.932$

where losses are expressed in percentage of urea-N applied and T is the time in hours.

We did an F test with the sum of squares due to deviations against the residual sum of squares of the alternative hypothesis. With the F value we determined if the models for the dry and the wet treatment were different (Table 8). The results showed that the models for the wet and dry treatments were significantly different only in replication 1. Differences observed in the second replication were not significant, and, as it was expected, there were no significant differences in replications 3 and 4 .

Differences in the rate of NH_3 loss between treatments were tested using the same method with which we compared cumulative NH_3 losses between treatments by replication.

The rate of NH_3 loss was calculated as the amount of NH_3-N from urea-N in percentage divided by the time-interval (12 hours). The null hypothesis was that one model for both treatments described the rate of loss over time. The alternative hypothesis was that the rate of loss should be described by two separate models, one for each treatment. The models used were :

Ho, Null Hypothesis

Log (Rate) = -4.80 + 1.63 Log (Time) $R^2=0.83^*$

Ha, Alternative Hypothesis

Wet air treatment

Log (Rate) = -4.53 + 1.49 Log (Time) $R^2=0.93^*$

Dry air treatment

Log (Rate) = -5.13 + 1.80 Log (Time) $R^2=0.76^*$

where rate is expressed as percentage of NH_3-N per hour and time in hours.

The lower coefficient of regression (R^2) of the dry air treatment model is due to the high rates found in replication 1, that increased the variability in the data. The calculated F value was not significant, indicating that there was no difference between the wet air and the dry air treatment in the rate of ammonia loss over time (Table

9).

Urea transformations in soil

The distribution of NH_4^+-N, NO_3^--N, pH, and urea-N with depth for each replication is shown in Figures 4, 5, 6, and 7 respectively.

The pattern of NH_4^+-N distribution is similar for the four replications. There was a greater concentration of ammonium at the surface in the dry air treatment due to the higher rate of soil water evaporation compared to the wet air treatment. In the wet air treatment, the concentration of NH_4^+-N was lower at the surface because of deeper diffusion of urea prior to hydrolysis, and also due to volatilization and nitrification. The NH_4^+-N concentration increased between 0.5 and 2 cm that is the zone of urea diffusion and higher pH. Below 2 cm, the concentration of NH_4^+-N dropped because of nitrification and diffusion. This NH_4^+-N concentration pattern for surface applications of urea was also reported by Singh and Nye (1986). Differences in total ammonium between treatments agreed with the total amount of urea-N hydrolyzed in each case (Table 2). The amount of NH_4^+-N observed in the controls were considered negligible compared to the fertilized soil chambers.

The distribution of NO_3^--N with depth also showed a

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similar pattern for the four replications. Accumulation of NO_3^--N at the surface occurred in the dry air treatment because of the high rate of evaporation.The distribution in the wet treatment clearly indicates where nitrification occurred. There was more accumulation of NO_3^--N at the surface and around 2 cm depth. In between these two zones of accumulation of nitrate the pH was higher than 8 because of urea hydrolysis. Wetselaar et al (1972) observed that values of pH higher than 8 inhibited nitrification. Darrah et al (1986) reported that the relative nitrification rate decreased at pH higher than 8 in a Begbroke sandy loam. Singh and Beauchamp (1988) also found that nitrification occurred 2 cm away from a urea layer where the pH dropped below 8. The amount of nitrate in the control chambers was low except in replication 1 in which nitrate accumulated at the surface due to evaporation. The percentage of urea-N nitrified was slightly higher in the wet air treatment than in the dry one, but this difference was not statistically significant (Table 2).

The pH decreased slightly at the soil surface because of the volatilization of ammonia. For each molecule of NH_3 volatilized, approximately one H^+ ion is released in the soil solution, thereby decreasing the pH. The distribution of pH with depth was similar for the four replications. The fertilized dry treatment showed an increase of pH

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between 0.5 to 1.5 cm due to urea hydrolysis. In the fertilized wet treatment the region of high pH extended from 0.5 to 2 cm due to a deeper diffusion of urea. Below 1.5-2 cm, the pH dropped due to nitrification and at the bottom of the soil chamber approached the original soil value (around 6.35). The pH of the control chambers increased from 6-6.4 in the surface to 6.8-7.4 near the bottom. The lower values at the top might have been due to nitrifier activity.

As already mentioned, urea-N diffused deeper in the wet treatment than in the dry one. This deeper diffusion could have been due to two reasons. First, the higher soil water evaporation of the dry treatment could cause accumulation of urea at the surface due to mass flow. Second, in replications 1 and 2 the greater soil water content of the wet air treatment might have allowed faster diffusion of urea into the soil. Sadeghi et al (1989) found that the molecular diffusion coefficient of urea in soil can be estimated by knowing the relative water content (volumetric water content/porosity). They found that the urea diffusion coefficient increased exponentially with the relative water content in seven soils.

The results of this research were not conclusive and showed that NH_3 volatilization is a complex process as demonstrated by several authors. Experimental conditions

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should be strictly controlled even at the laboratory. A next step in this research could be to introduce new modifications in our laboratory apparatus in order to have better control of the soil water potential in the chamber. Finally, validation of the data in the field will be necessary.

Table 1. Evaporation and Ammonia Volatilization at the end of the experiment.

Replication and Treatment	Time	Evaporation	NH$_3$-N Volatilization		
	hours	mL	% of added	% of hydrolyzed (1)	% of hydrolyzed (2)
1					
Dry air	184	21.0	17.3	26.2	30.1
Wet air	184	12.5	9.1	13.0	14.0
2					
Dry air	226	30.0	12.1	17.3	21.0
Wet air	226	6.0	8.3	9.6	11.6
3					
Dry air	239	33.2	8.7	12.4	12.5
Wet air	239	9.9	8.4	10.3	9.2
4					
Dry air	253	34.7	11.3	13.8	13.0
Wet air	253	8.5	11.4	11.9	11.8
Mean					
Dry air		29.7	12.4	17.4	19.2
Wet air		9.2	9.3	11.2	11.9
		*	NS	NS	NS

(1) Urea-N hydrolysis calculated by appearance of ammonium-N, nitrate-N, and ammonia-N.
(2) Urea-N hydrolysis calculated by disappearance of urea-N.

NS No significant differences at the 0.05 probability level.
*   Significant differences at the 0.05 probability level.

Table 2. Urea-N hydrolysis, Urea-N nitrification, and Urea-N accounted for at the end of the each replication.

Replication and Treatment	Urea-N hydrolyzed		Urea-N nitrified	Urea-N accounted for
	(1)	(2)		
	----------------- % ----------------------			
1 Dry air	58	66	3	91
Wet air	66	70	5	96
2 Dry air	58	70	11	87
Wet air	69	86	15	83
3 Dry air	70	70	26	99
Wet air	91	81	29	110
4 Dry air	86	82	36	105
Wet air	89	96	30	93
Mean Dry air	68	72	19	96
Wet air	79	83	20	95
	NS	*	NS	NS

(1) Urea-N hydrolysis calculated by appearance of ammonium-N, nitrate-N, and ammonia-N.
(2) Urea-N hydrolysis calculated by disappearance of urea-N.

NS No significant differences at the 0.05 probability level.
* Significant differences at the 0.05 probability level.

Table 3. Soil Water Content, pH, NH_4^+-N, NO_3^--N, Urea-N in the soil at the end of replication 1.

Depth	Soil Water Content	pH	NH_4^+-N	NO_3^--N	Urea-N
mm	kg/kg		--------mg/kg soil---------		

Wet Air Treatment Fertilized

Depth	Soil Water Content	pH	NH_4^+-N	NO_3^--N	Urea-N
0-2	0.16	7.9	295	31	827
2-5	0.16	8.3	344	24	407
5-10	0.17	8.6	318	24	270
10-15	0.17	8.7	279	27	76
15-20	0.17	8.5	252	33	30
20-30	0.18	7.7	145	26	0
30-40	0.19	6.4	28	12	0
40-50	0.20	6.6	1	5	0

Dry Air Treatment Fertilized

Depth	Soil Water Content	pH	NH_4^+-N	NO_3^--N	Urea-N
0-2	0.14	8.1	290	41	693
2-5	0.14	8.4	272	31	355
5-10	0.14	8.6	255	27	110
10-15	0.14	8.5	196	25	8
15-20	0.14	8.2	160	19	0
20-30	0.14	6.9	39	7	0
30-40	0.15	6.8	2	3	5
40-50	0.17	7.1	1	1	0

Wet Air Treatment Check

Depth	Soil Water Content	pH	NH_4^+-N	NO_3^--N	Urea-N
0-2	0.17	6.4	4	20	-
2-5	0.16	5.8	4	17	-
5-10	0.17	6.6	4	9	-
10-15	0.17	6.6	3	8	-
15-20	0.17	6.7	3	7	-
20-30	0.17	6.8	3	5	-
30-40	0.17	6.9	1	4	-
40-50	0.18	7.1	1	1	-

Dry Air Treatment Check

Depth	Soil Water Content	pH	NH_4^+-N	NO_3^--N	Urea-N
0-2	0.12	6.3	3	54	-
2-5	0.12	6.8	5	7	-
5-10	0.12	7.0	3	3	-
10-15	0.13	7.0	3	2	-
15-20	0.13	7.1	3	2	-
20-30	0.13	7.2	2	2	-
30-40	0.14	7.2	2	1	-
40-45	0.17	7.4	2	0	-

Table 4. Soil Water Content, pH, NH_4^+-N, NO_3^--N, Urea-N in the soil at the end of replication 2.

Depth	Soil Water Content	pH	NH_4^+-N	NO_3^--N	Urea-N
mm	kg/kg		--------mg/kg soil---------		
Wet Air Treatment Fertilized					
0-2	0.17	8.0	245	47	215
2-5	0.17	8.3	253	43	188
5-10	0.18	8.3	313	65	112
10-15	0.19	8.1	243	56	29
15-20	0.21	7.8	227	88	14
20-30	0.21	6.0	92	65	0
30-40	0.21	5.8	25	21	0
40-50	0.20	6.4	3	8	0
Dry Air Treatment Fertilized					
0-2	0.14	7.8	287	116	696
2-5	0.14	8.2	275	77	275
5-10	0.15	8.2	235	61	75
10-15	0.15	7.5	173	55	0
15-20	0.14	6.3	73	31	0
20-30	0.14	6.1	19	12	0
30-40	0.16	6.7	0	2	0
40-50	0.18	6.9	0	0	0
Wet Air Treatment Check					
0-2	0.17	6.1	1	4	-
2-5	0.16	6.2	1	3	-
5-10	0.17	6.3	0	2	-
10-15	0.17	6.3	0	2	-
15-20	0.17	6.4	0	2	-
20-30	0.18	6.5	0	2	-
30-40	0.19	6.7	0	1	-
40-50	0.19	6.9	0	0	-
Dry Air Treatment Check					
0-2	0.10	5.9	1	25	-
2-5	0.10	6.4	0	2	-
5-10	0.11	6.6	0	1	-
10-15	0.12	6.7	0	0	-
15-20	0.12	6.8	0	1	-
20-30	0.13	6.9	1	1	-
30-40	0.15	7.0	1	0	-
40-45	0.23	7.1	2	0	-

Table 5. Soil Water Content, pH, NH_4^+-N, NO_3^--N, Urea-N in the soil at the end of replication 3.

Depth	Soil Water Content	pH	NH_4^+-N	NO_3^--N	Urea-N
mm	kg/kg		---------mg/kg soil----------		
Wet Air Treatment Fertilized					
0-2	0.17	7.7	309	100	339
2-5	0.19	8.0	314	94	280
5-10	0.17	8.1	305	94	137
10-15	0.18	7.9	280	106	49
15-20	0.18	7.2	244	120	10
20-30	0.19	5.5	129	112	3
30-40	0.20	5.4	33	58	2
40-50	0.19	6.4	5	16	0
Dry Air Treatment Fertilized					
0-2	0.17	7.6	277	192	583
2-5	0.17	7.9	326	183	525
5-10	0.18	7.8	280	151	175
10-15	0.18	6.7	181	127	11
15-20	0.18	5.2	116	99	0
20-30	0.18	5.1	32	54	0
30-40	0.19	6.2	2	10	0
40-50	0.20	6.8	1	3	0
Wet Air Treatment Check					
0-2	0.14	6.2	2	7	-
2-5	0.15	6.5	0	1	-
5-10	0.15	6.6	1	0	-
10-15	0.15	6.7	0	0	-
15-20	0.15	6.7	0	0	-
20-30	0.16	6.8	0	0	-
30-45	0.17	6.8	0	0	-
Dry Air Treatment Check					
0-2	0.16	6.1	1	8	-
2-5	0.15	6.4	0	4	-
5-10	0.16	6.5	0	2	-
10-15	0.17	6.6	0	2	-
15-20	0.17	6.7	7	2	-
20-30	0.16	6.8	0	1	-
30-40	0.17	6.8	0	1	-
40-50	0.18	7.1	0	0	-

Table 6. Soil Water Content, pH, NH_4^+-N, NO_3^--N, Urea-N in the soil at the end of replication 4.

Depth	Soil Water Content	pH	NH_4^+-N	NO_3^--N	Urea-N
mm	kg/kg		---------mg/kg soil--------		
Wet Air Treatment Fertilized					
0-2	0.20	7.5	314	120	83
2-5	0.20	8.0	344	114	66
5-10	0.20	8.0	296	108	24
10-15	0.21	7.7	264	121	9
15-20	0.21	6.9	203	132	2
20-30	0.23	5.1	96	115	1
30-40	0.23	5.2	28	52	1
40-50	0.22	6.2	7	17	0
Dry Air Treatment Fertilized					
0-2	0.21	7.4	372	373	331
2-5	0.21	7.8	339	257	247
5-10	0.22	7.4	260	181	75
10-15	0.22	6.2	168	142	11
15-20	0.23	5.0	98	113	6
20-30	0.23	4.9	21	55	4
30-40	0.24	5.9	5	19	3
40-50	0.23	6.7	0	5	0
Wet Air Treatment Check					
0-2	0.18	6.1	1	1	-
2-5	0.18	6.3	1	1	-
5-10	0.18	6.4	1	1	-
10-15	0.19	6.5	1	0	-
15-20	0.19	6.5	0	1	-
20-30	0.19	6.6	0	1	-
30-45	0.19	6.8	0	1	-
Dry Air Treatment Check					
0-2	0.23	6.4	2	5	-
2-5	0.23	6.3	3	4	-
5-10	0.25	6.4	1	3	-
10-15	0.26	6.4	1	3	-
15-20	0.26	6.5	1	2	-
20-30	0.26	6.8	0	2	-
30-40	0.24	6.8	1	1	-
40-45	0.21	6.9	1	0	-

Table 7. Analysis of variance for ammonia volatilization calculated as percentage of urea-N applied.

Source of variation	Degrees of freedom	Sum of squares	Mean Squares	F value
Treatment	1	18.63	18.63	2.46 NS
Blocks	3	23.24	7.74	
Error	3	22.66	7.55	
Total	7	64.53		

NS No significant differences at   level = 0.05.

Table 8. Test of null hypothesis for cumulative NH_3 losses by replication.

Replication	Ho		Ha		Deviation		F value
	df	SS	df	SS	df	SS	
1	31	180.9	15	42.4	16	138.5	3.06*
2	37	76.1	18	38.0	19	38.1	0.95
3	39	38.5	19	37.2	20	1.3	0.03
4	41	41.3	20	40.9	21	0.3	0.01

* Significant differences at   level = 0.05.

Table 9. Test of null hypothesis for rate of NH_3 volatilization over time.

Ho		Ha		Deviation		F value	
df	SS	df	SS	df	SS		
148	10.4	74	9.9	74	0.5	0.05	NS

NS No significant differences at   level = 0.05.
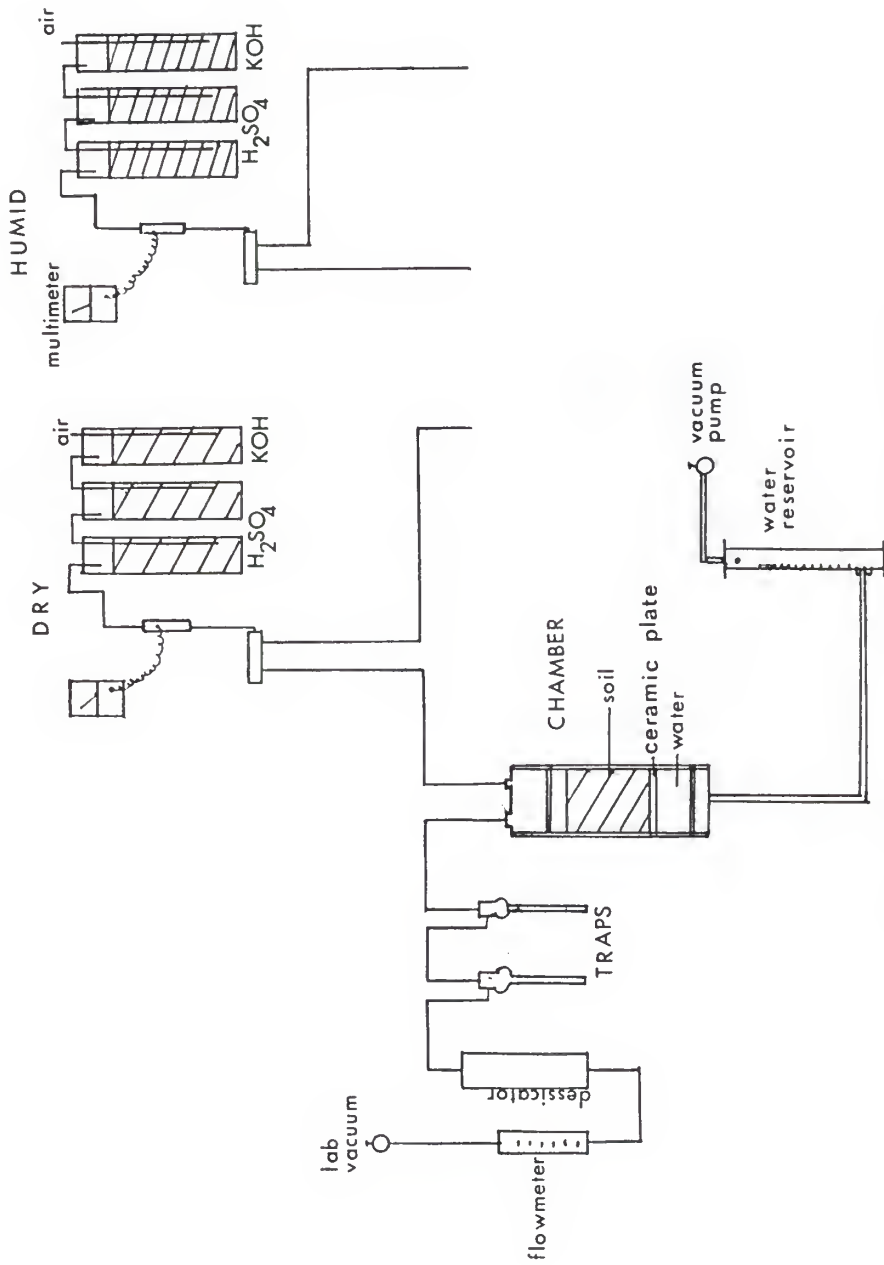
Fig.1   Schematic representation of the laboratory apparatus
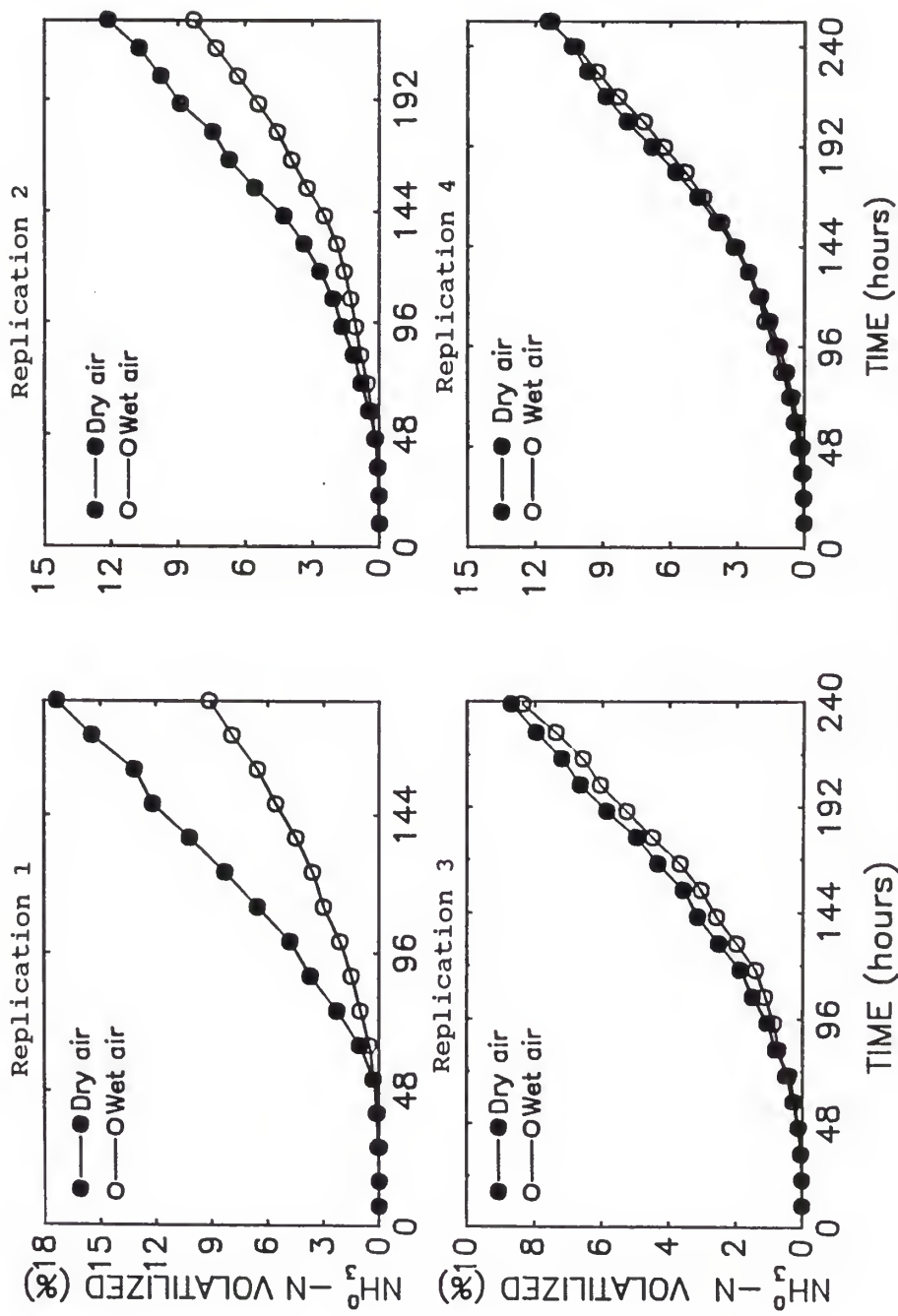
Fig.2 Cumulative ammonia volatilization over time
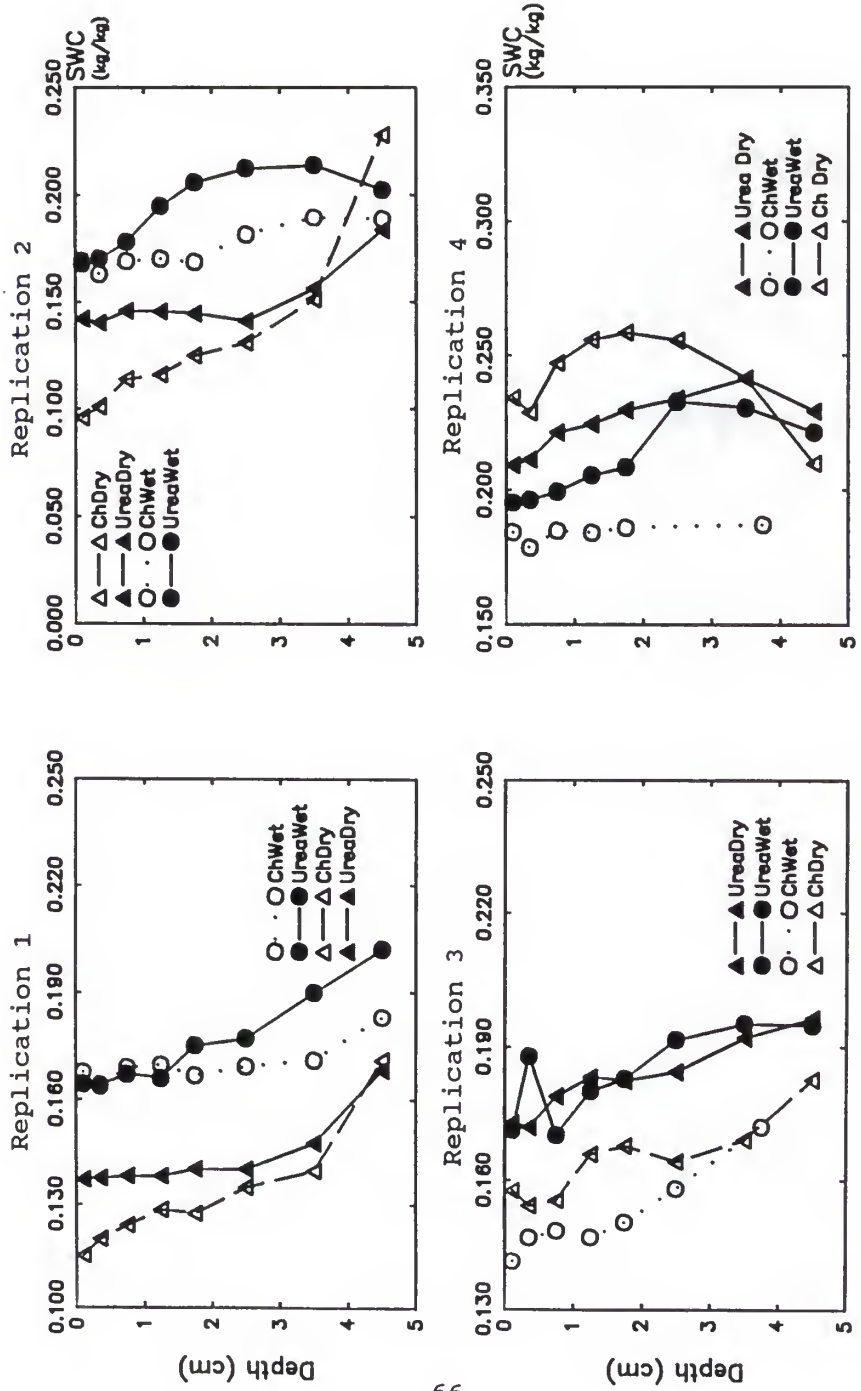
Fig.3 Profile of soil water content at the end of each replication
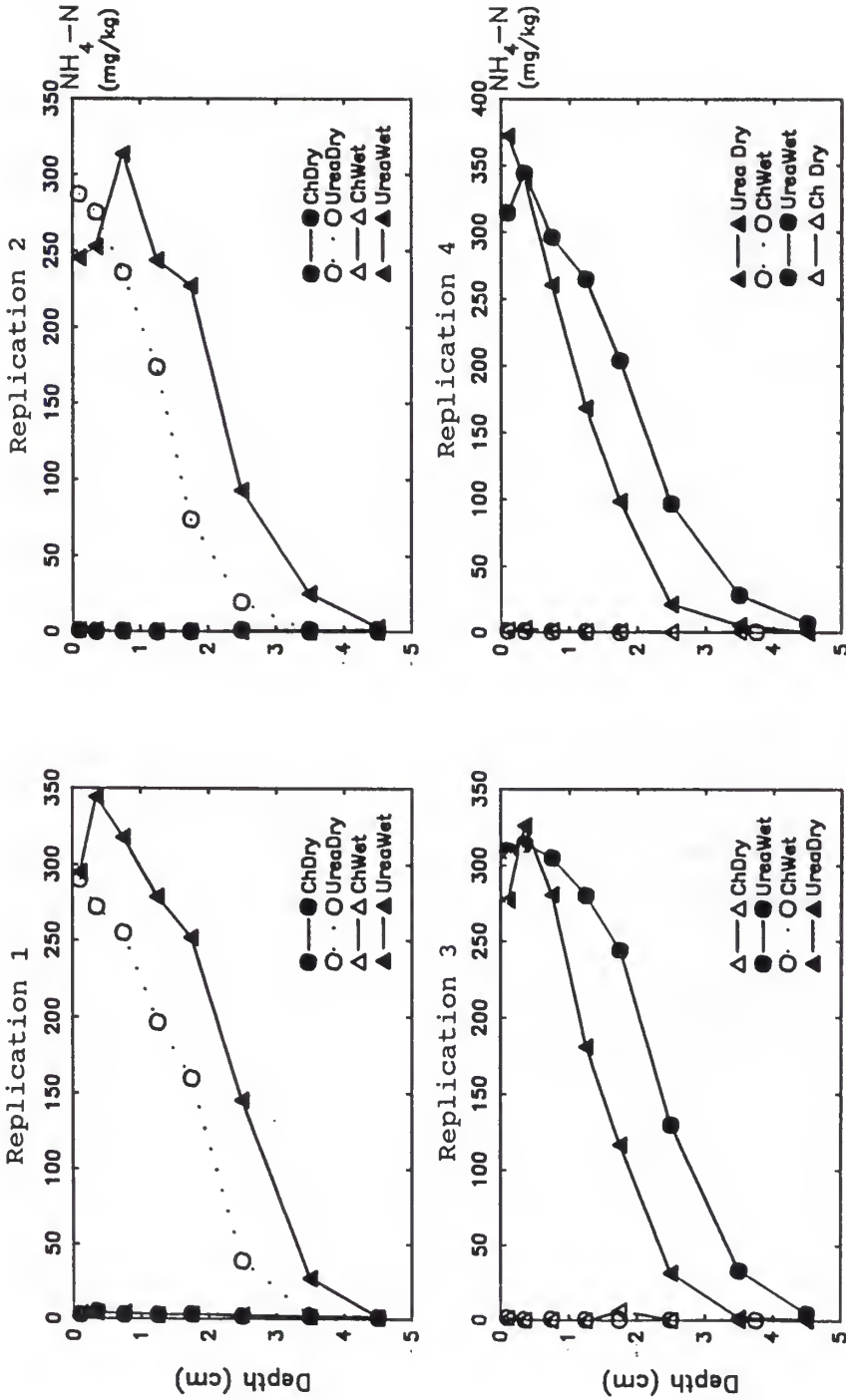
Fig. 4 Concentration profile of ammonium-N at the end of each replicattion

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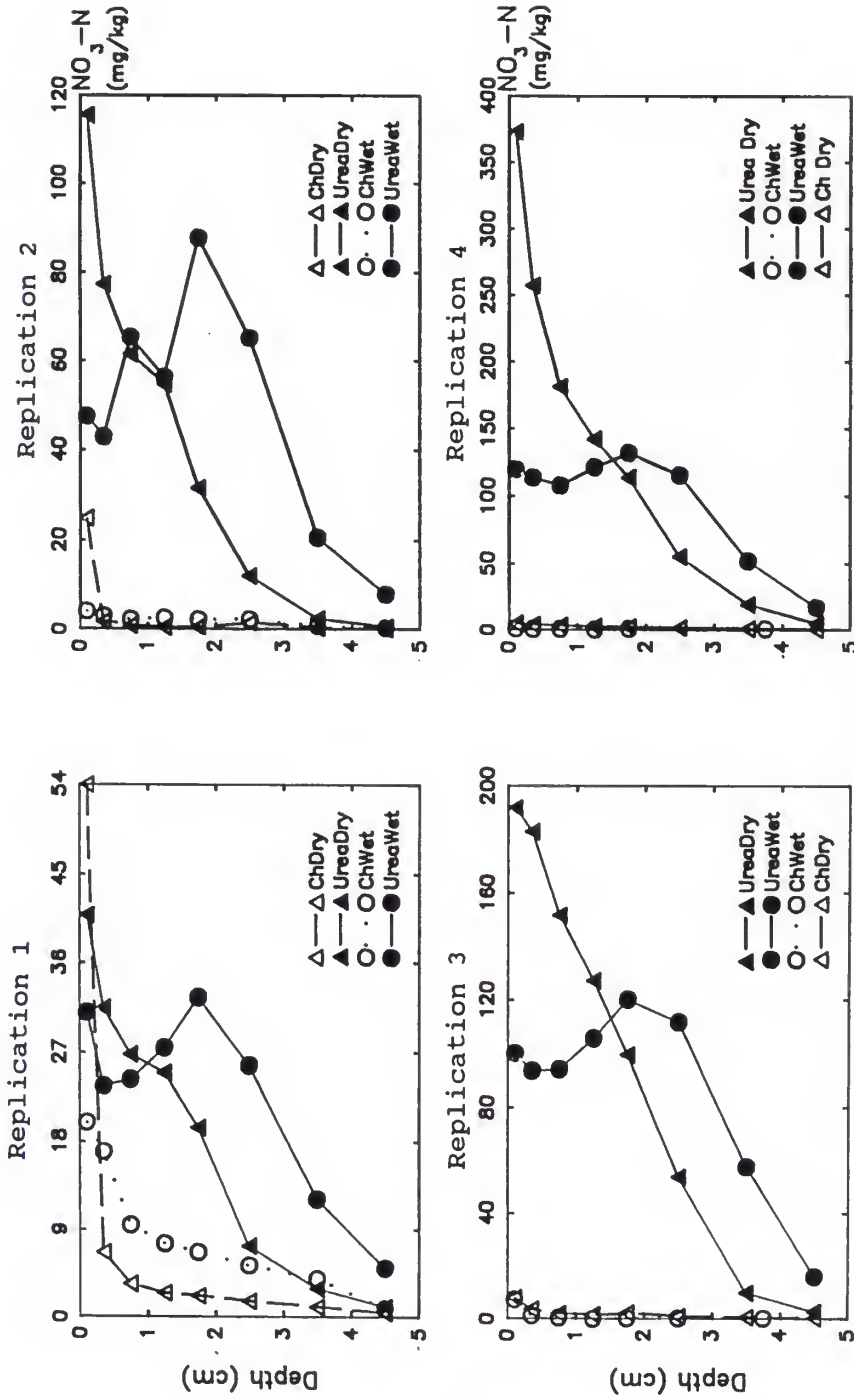
Fig.5 Concentration profile of nitrate-N at the end of each replication

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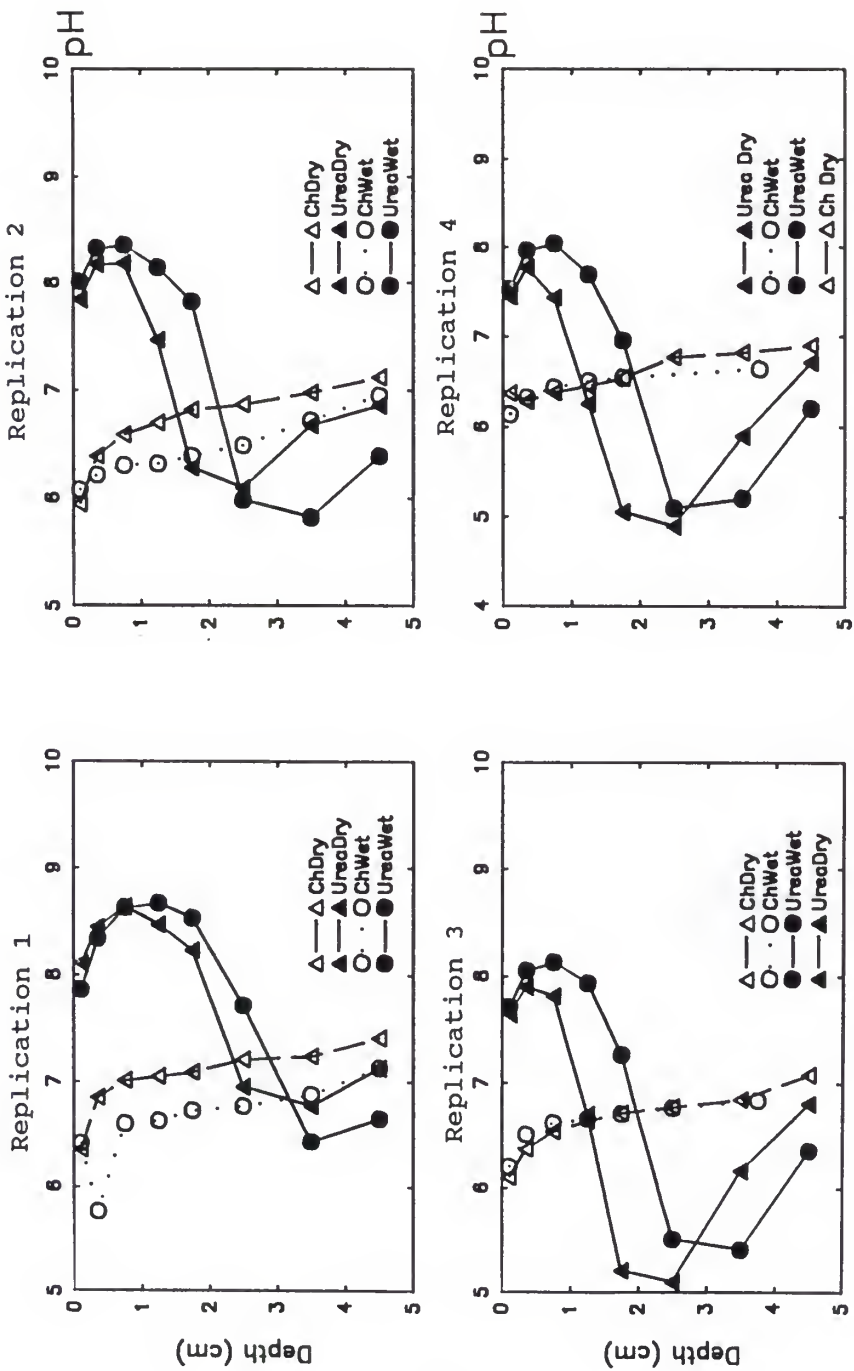
Fig.6 Profile of pH at the end of each replication

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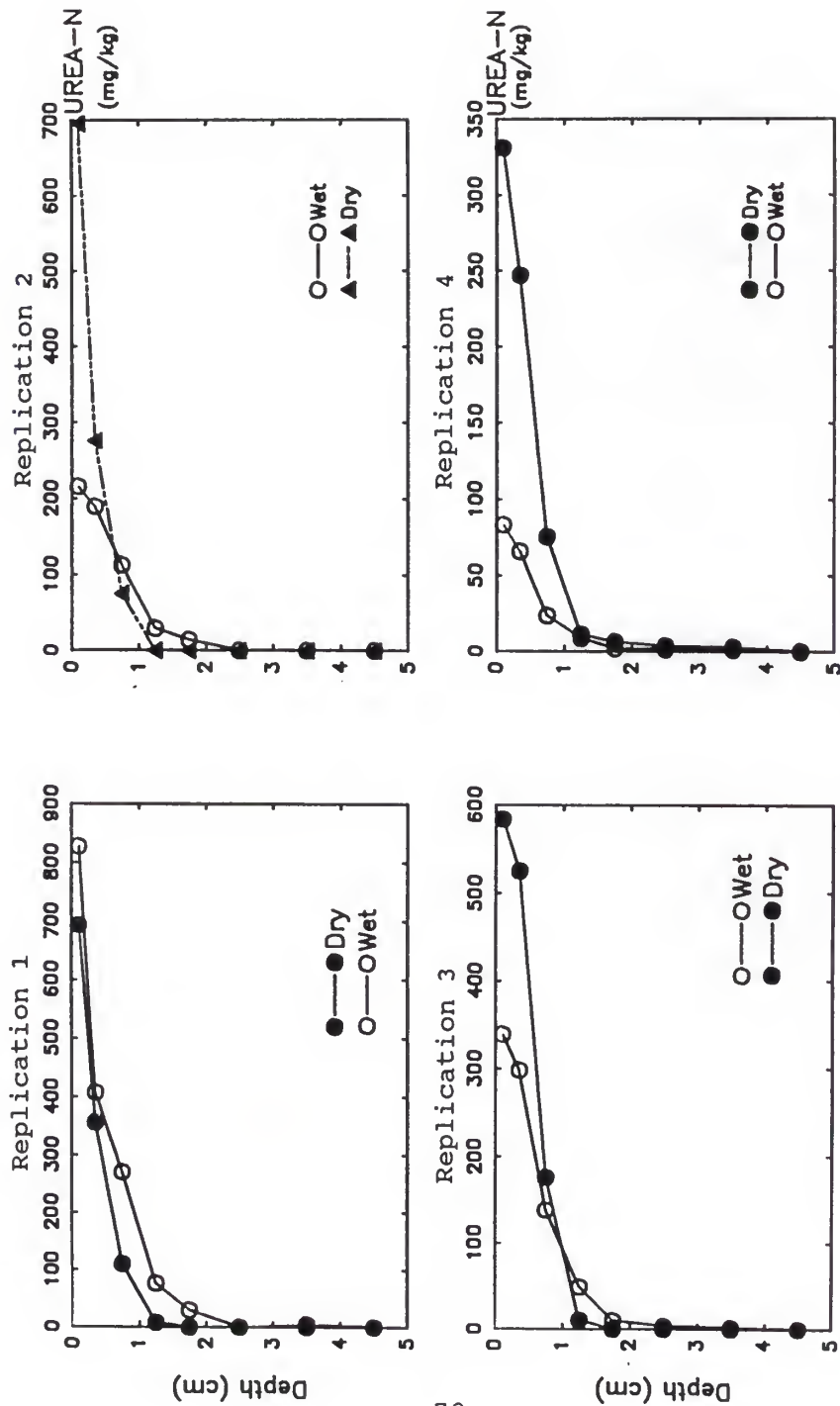
Fig.7 Concentration profile of urea-N at the end of each replication

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Chapter 3

Effect of soil water potential on urea hydrolysis

Urea applied to soil undergoes a rapid hydrolysis according to the following reaction :

$$CO(NH_2)_2 + 2\ H_2O + H^+ \xrightleftharpoons[urease]{} 2\ NH_4^+ + HCO_3^-$$
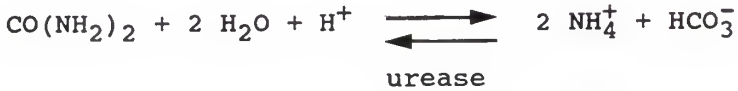
The rate of this reaction depends on the number of active urease molecules and the factors that affect the activity of urease. Urease activity is affected by pH, substrate concentration, soil temperature, and soil water content (Kissel and Cabrera, 1988).

Different results have been obtained in studies of the effect of water content on the rate of urea hydrolysis in soil. In most cases, urease activity has not been affected appreciably by water content, but other studies have shown that the rate of hydrolysis increased or decreased by increasing soil water content (Bremner and Mulvaney, 1978).

Kissel and Cabrera (1988) found that there was no good relationship between urease activity and gravimetric water content in soils that varied widely in texture. By con-

verting soil water contents to soil water potentials, they found a much better general relationship between urease activity and water potential. However, they noticed that there was a lack of data at the very dry water contents that routinely occurs at the soil surface under field conditions.

The objective of this research was to evaluate the effect of various soil water potentials on urea hydrolysis. We approached the study in two different ways. In Experiment I a constant amount of urea-N per mass of soil was used. Since urea is hydrolyzed when it is in solution, in Experiment II we maintained a constant initial concentration of urea-N in soil solution across a wide range of soil water contents.

Materials and Methods

Surface soil samples (0-0.15 m) were collected from areas mapped as Kahola silt loam (fine-silty, mixed, mesic, Cumulic Hapludolls) and Smolan silt loam (fine, montmorillonitic, mesic, Pachic Argiustolls) at the North Agronomy Farm; Haynie very fine sandy loam (coarse-silty, mixed, calcareous, mesic, Typic Udifluvents) and Reading silt loam (fine, mixed, mesic, Typic Argiustolls) at the Ashland Agronomy Farm of Kansas State University; and

Captina silt loam (fine-silty, mixed, mesic, Typic Fragiu-
dults) at the Agronomy Farm of the University of Arkansas
(Table 1). Particle size analysis was done by the hydrome-
ter method (Day, 1956) to determine clay content and by
sieving the dispersed soil sample through a 50 um sieve to
determine sand content. Silt content was determined by
difference. Total carbon in soil was determined by using a
LECO Carbon Analyzer (LECO Corp., St. Joseph, Michigan).
Soil pH was measured in a 1:1 soil:water ratio paste with
a combination microelectrode and an Orion 701A pH meter.

After collection, the soils were stored at room temper-
ature (25°C). Immediately before the experiment, the soils
were passed through a 2 mm sieve, leached with a N-free
solution to decrease the level of NO_3^- and NH_4^+ (Cabrera
and Kissel, 1988), and again passed through a 2 mm sieve.
Then the soils were mixed with the necessary amount of
$Ca(OH)_2$ to bring the pH to approximately 8.2. This pH was
indicated by Bremner and Mulvaney (1978) as optimum for
urease activity. Finally the soils were incubated for one
week at 5 ^{o}C. Two soils, Kahola and Reading, were also
studied at their original pH. They were prepared in the
same way but no $Ca(OH)_2$ was added. The amount of $Ca(OH)_2$
added and the pH at the end of the incubation period for
the five soils are showed in Table 2.

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For each soil, six different levels of soil water content were evaluated; these were obtained by drying the soil for different periods of time. For each of the six soil water levels, soil was incubated with urea and without urea (control), each replicated three times, resulting in a total of 36 experimental units for each soil (6 water levels * 3 replications * 2 treatments). Moist soil in amounts equivalent to 20 g of oven-dry soil, was placed in 125-mL square bottles and 1200 ug urea-N / g dry soil was added to soil at each level of moisture. In Experiment II, the amount of urea-N added was calculated as a function of the amount of water in soil as follows

$$\text{Urea} = \text{SWC} * \text{W} * 40000 \text{ ug urea-N } g^{-1} * \text{Factor}$$

where   Urea = amount of urea added, g

SWC = soil water content, g water / g soil

W = weight of oven-dry soil, 20g

Factor = 10^{-6} g/ug * 2.174 g urea/ g urea-N

The concentration of urea-N in the soil solution (40000ug urea-N/g soil), was selected by estimating the concentration around a urea fertilizer granule applied to the soil. Ultra pure crystalline urea (Schwarz/Mann Biotech, Cleveland, Ohio) was uniformly mixed with the soil

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using a glass rod. The rods were left in the bottles during the incubation period and the extraction.

After adding the urea, the square bottles (fertilized and controls), were stoppered, weighed, and incubated at 35 °C for 24 hours. At the end of the 24 hour incubation, the square bottles were weighed again in order to check for any water loss during incubation. No differences were observed between initial and final weights. Enough water was added to make a 1:1 paste and pH was measured with a combination microelectrode and an Orion 701A pH meter. After pH measurement, 50 mL of 3.2 M KCl-8 mg kg^{-1} PMA solution was added to the flask and the flask shaken for 30 minutes. The soil suspension was then transferred to a Buchner funnel under suction, filtered through Whatman # 41 filter paper, and leached with 15 mL of 2 M KCl-PMA solution. The leachate was diluted to 100 mL with 2 M KCl-PMA solution and frozen until analysis could be performed. The leachate was analyzed colorimetrically for urea-N using the procedure of Douglas and Bremner (1970), and for ammonium and nitrate using Technicon Industrial Systems procedures (1977a and 1977b). All analysis were performed on a Technicon Autoanalyzer II system.

We measured the recovery of urea-N in triplicate in the highest and lowest level of soil water content immediately

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after adding the fertilizer. After placing the 20 g of oven-dry soil in the square bottle, we added 50 mL of 2 M KCl-PMA and then the urea. These bottles were extracted as described above and analyzed for urea-N, ammonium-N and nitrate-N. Values of ammonium-N and nitrate-N were averaged and considered initial values for the soil. Urea-N recoveries were higher than 96% in all cases.

The rate of urea hydrolysis was calculated in two different ways : i) by accounting for disappearance of urea-N, and ii) by accounting for appearance of NH_4^+-N and NO_3^--N after subtracting the amounts of NH_4^+-N and NO_3^--N observed in the controls at the end of the incubation. In order to obtain a general relationship between soil water potential and the rate of urea hydrolysis, we defined a relative rate of urea hydrolysis. This relative rate was calculated as the average rate observed at a particular soil water potential divided by the maximum average rate observed. The relative rate was also calculated by disappearance of urea-N (DRR), and by appearance of hydrolysis products (ARR).

The N ammonified in the control treatments during the 24 hours-incubation period was calculated as the difference between final NH_4^+-N + NO_3^--N and initial NH_4^+-N + NO_3^--N. The N nitrified in the controls was calculated as

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the difference between NO_3^--N at the beginning and at the end of the incubation period. The urea-N accounted for was calculated as follows :

$$Urea_{AC} = \frac{Urea_F + (Am_E - Am_{CE}) + (Nit_E - Nit_{CE})}{Urea_B} * 100$$

where

$Urea_{AC}$ = Urea-N accounted for, %

$Urea_F$ = Urea-N at the end of incubation, mg/kg

Am_E = NH_4^+-N at the end of incubation, mg/kg

Am_{CE} = NH_4^+-N in the control at the end of
incubation, mg/kg

Nit_E = NO_3^--N at the end of incubation, mg/kg

Nit_{CE} = NO_3^--N in the control at the end
of incubation, mg/kg

$Urea_B$ = Urea-N added at the beginning of
incubation, mg/kg

Soil moisture characteristic curves

The soil moisture characteristic curves were developed using a Decagon SC-10 thermocouple psychrometer (Decagon Devices Inc., NW 800 Fisk, Pullman WA 99163). The psychrometer was calibrated for the measurement of water

potential using KCl solutions of known molality. The calibration curve converts readings (uV) to water potential (MPa) :

Reading = $0.1086 - 0.0598$ WP $\qquad R^2 = 0.999$

The soil moisture characteristic curves were prepared by drying soil to different water contents. Soil water content was determined by oven-drying the samples at 105 $^{\circ}$C for 24 hours and then taking dry weights. It was determined that the samples reached constant weight after a drying period of 24 hours.

Data of soil water potential and soil water content were fitted using a double logarithmic relationship. Equations fitted for each soil were as follows :

Kahola

log SWC = $-0.933 - 0.308$ log SWP $\qquad R^2 = 0.96$

Captina

log SWC = $-1.284 - 0.447$ log SWP $\qquad R^2 = 0.96$

Smolan

log SWC = $-0.850 - 0.246$ log SWP $\qquad R^2 = 0.99$

Reading

log SWC = $-0.958 - 0.294$ log SWP $\qquad R^2 = 0.99$

Haynie

log SWC = $-1.267 - 0.404$ log SWP $\qquad R^2 = 0.93$

where   SWC = soil water content, g water / g soil

      SWP = soil water potential, MPa

Results and Discussion

Experiment I

The absolute and relative rate of urea hydrolysis for each soil and level of soil water potential are shown in Table 3. The urea-N, and pH at the end of the incubation, and NO_3^--N and NH_4^+-N before and after the incubation are shown in Table A1. The mean urea-N accounted for in the seven soils was 94.7 ± 5.5 %. The percentage of urea-N hydrolyzed varied between 0.5 and 43.5% depending on soil and soil water potential level.

A nonlinear procedure (SAS, 1985) was used to fit a model between relative rate of urea hydrolysis and soil water potential. Equations fitted were :

a) Relative rate calculated by disappearance of urea-N (DRR)

DRR = 0.909*exp(0.085*SWP) $R^2=0.55^*$

b) Relative rate calculated by appearance of hydrolysis products (ARR)

ARR = 0.955*exp(0.170*SWP)) $R^2=0.90^*$

where SWP is the soil water potential in MPa (Figures 1 and 2).

In order to know if these general models represent the

effect of soil water potential on the relative rate of urea hydrolysis for all the soils, we conducted a test comparing the general models with the models for each individual soil. The null hypothesis (Ho) to test was that one model can describe the effect of soil water potential for all soils. The alternative hypothesis (Ha) was that one model cannot describe the effect of soil water potential for all the soils, i.e. the effect of soil water potential should be described by a separate model for each soil. The residual sum of squares for the alternative hypothesis was calculated by adding the residual sum of squares of the models for each soil. The difference between the residual sum of squares of the null and the alternative hypothesis gave an estimation of the residual sum of squares due to deviations from the null hypothesis. The general form of the models was :

Relative Rate = (A * Exp (B* SWP)

where SWP is the soil water potential in MPa. The coefficients A, and B for the individual soils are shown in Table 4. We did an F test with the sum of squares due to deviations against the residual sum of squares of the alternative hypothesis. In both cases, by calculating the

rate by disappearance of urea-N or by appearance of hy-
drolysis products, the individual models for each soil
showed a significantly better fit than the general model
(Table 5). This means that the effect of soil water poten-
tial on relative rate of urea hydrolysis depends on the
soil.

In Reading silt loam at its original pH, there was
considerable variability in the data and we could not get
a good fit (Table 4). In the other soils and also in the
general model, it was possible to obtain a better fit with
ARR than DRR. The relative rate could have been affected
by a concentration effect. As we dried the soil, the
volume of soil solution decreased and as the amount of
urea-N added remained constant, the concentration in soil
solution increased. This effect will be discussed later.
The rate of hydrolysis calculated by appearance of hydrol-
ysis products was generally lower than the rate calculated
by disappearance. This suggests that N was lost from the
hydrolysis products NH_4^+-N, NO_2^--N, or NO_3^--N.

The amount of N ammonified in the control treatments
during the 24 hour incubation-period was generally nega-
tive, indicating that there were losses of N (Table 6). No
relationship could be found between N ammonified and soil
water potential. The amount of N nitrified was positive,

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generally with a tendency to be greater at higher soil water potentials. The relationship found was :

$$\text{N nitrified} = 1.759 * \exp (-0.265 * \text{SWP}) \qquad R^2 = 0.511^*$$

where N nitrified was in mg N nitrified $* \text{kg soil}^{-1}$, and SWP is the soil water potential.

Nitrogen would have been lost from soil as a gas. There are three possible mechanisms of gaseous losses : biological denitrification, ammonia volatilization, and chemodenitrification. Biological denitrification could not be important in this case because it requires poor aeration conditions, something that did not happen in our experiment. Chemodenitrification, the loss of N as NO_2 from HNO_2 decomposition, was suggested as a possible cause of N loss in soils (Steen and Stojanovic, 1971), but Bundy and Bremner (1974) showed that N deficits observed in studies with urea are not largely due to chemodenitrification and they suggested ammonia volatilization and ammonium fixation as possible causes of these N deficits. In our experiment the high pH suggested that ammonia volatilization might have been the main cause of the N deficit. Another possible cause might have been ammonium fixation.

The relative rate of urea hydrolysis was related to the

soil water content by the following equations :

$$DRR = 1.488 + 0.726 \log SWC \qquad R^2 = 0.60$$

$$ARR = 1.598 + 0.882 \log SWC \qquad R^2 = 0.59$$

where SWC is the soil water content in g water / g soil
(Figures 3 and 4). As discussed by Kissel and Cabrera
(1988), no good general relationship has been found be-
tween urease activity and gravimetric water content.

The absolute rate of urea hydrolysis was greater in the
limed Kahola and Reading soils than in the same soils at
the original pH (Table 3). Similar results were reported
by Bremner and Mulvaney (1978). In order to know if the
initial soil pH had any effect on the response of urea
hydrolysis to soil water potential, we evaluated the
models for Kahola and Reading at each soil pH against a
pooled model for each soil. The null hypothesis (Ho) was
that one model can explain the effect of soil water poten-
tial on urea hydrolysis at any soil pH. The alternative
hypothesis (Ha) was that the effect of soil water poten-
tial on urea hydrolysis should be described by a separate
model for each soil pH. The individual models for each
soil and pH are shown in Table 4; and the pooled models
used for each soil were :

Reading

$$DRR = 0.947 * \exp (0.224 * SWP) \qquad R^2 = 0.20^*$$

$$ARR = 0.985 * \exp (0.270 * SWP) \qquad R^2 = 0.93^*$$

Kahola

$$DRR = 0.906 * \exp (0.042 * SWP) \qquad R^2 = 0.60^*$$

$$ARR = 0.950 * \exp (0.215 * SWP)) \qquad R^2 = 0.92^*$$

The F values obtained from the mean squares of the
deviations against the mean squares of the alternative
hypothesis were significant for the DRR in both soils, but
the F value was not significant for the ARR (Table 7). A
significant F value would suggest that the initial soil pH
had a significant effect on the response of urea hydroly-
sis to soil water potential. Since in this experiment we
found different results depending on which relative rate
was used, the results were not conclusive.

The rate and relative rate of urea hydrolysis for each soil and level of soil water potential are shown in Table 8. The means for the three replications of urea-N and pH at the end of the incubation, and for NO_3^--N and NH_4^+-N before and after the incubation are shown in Table A2. The mean urea-N accounted for was 93.1 ± 6.07 % for all seven soils. The percentage of urea-N hydrolyzed varied between 3.5 and 40.0% depending on the soil and level of soil water potential.

We fitted a model between relative rate of urea hydrolysis and soil water potential using a non linear procedure (SAS, 1985) (Figures 5 and 6). Equations fitted were :

DRR = 1.031 * exp(0.706 * SWP)) R^2 = 0.83[*]

ARR = 0.94 * exp(0.487 * SWP)) R^2 = 0.75[*]

We conducted a test comparing the general model with the models for each individual soil as it was described for Experiment I. In spite of the high coefficient of correlation (R^2) found in both general models, the F values were significant indicating that the individual models should be considered in describing relative rate-soil water potential relationships (Table 9). The coefficients for the models of each soil are shown in Table 10.

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In this experiment a better agreement was found between the relative rate calculated by disappearance of urea (DRR) and the one calculated by appearance of hydrolysis products (ARR). However, the loss of N in the control treatments during the incubation period was noted again, as observed for Experiment I. No relationship could be found between N ammonified in the control treatments and soil water potential, but the amount of N nitrified in the control treatments was related to the soil water potential by the following equation :

N nitrified = 1.865 * exp (0.568 * SWP) $R^2 = 0.66^*$

where N nitrified is in mg N per kg of soil and SWP is the soil water potential in MPa. The means of N mineralized and N nitrified in the control treatments by soil and level of soil water content are shown in Table 11.

The relationship found between urease activity and soil water content in this Experiment was much closer than in Experiment I and it was found to be linear in the range of soil water content studied (Figures 7 and 8):

DRR = -0.029 + (5.081 * SWC) $R^2 = 0.70^*$

ARR = -0.059 + (5.371 * SWC) $R^2 = 0.79^*$

The absolute rate of hydrolysis was greater in the limed Kahola and Reading soils than in the same soils at

the original pH (Table 8). The comparison of the models describing the effect of the soil water potential on urea hydrolysis at any soil pH and the models at each soil pH for Reading and Kahola showed that soil pH significantly affected the response of urea hydrolysis to soil water potential (Table 12). The pooled models fitted were :

Reading

$$DRR = 0.994 * exp(0.543 * SWP) \qquad R^2 = 0.87^*$$

$$ARR = 1.033 * exp(0.475 * SWP) \qquad R^2 = 0.92^*$$

Kahola

$$DRR = 1.197 * exp(1.047 * SWP) \qquad R^2 = 0.83^*$$

$$ARR = 0.940 * exp(0.353 * SWP) \qquad R^2 = 0.83^*$$

General Discussion

In Experiment II the urea-N concentration in soil solution was constant at 2.8M, whereas in Experiment I the concentrations varied depending on soil water content. In Captina and Haynie, urea-N concentrations ranged from 0.6 to 4.8M, in Kahola from 0.4 to 2.0M, in Reading from 0.4 to 0.8 (at original pH) or 3.0M (pH 8.24), and in Smolan from 0.4 to 1.7M. These variations in concentration would explain the differences observed in the absolute rate between both experiments at the higher soil water potentials. As the soil water potential decreased, the rates of both experiments approached each other because urea-N concentrations became similar.

The urea-N concentration in soil solution has been shown in many studies to affect the rate of urea hydrolysis, and as indicated earlier, it may have confounded the effect of soil water potential on urea hydrolysis rates thereby causing the poor fit between relative rate and soil water potential in Experiment I.

In order to know if there was a confounding of urea-N concentration on the response of urea hydrolysis to soil water potential, we compared the relative rates of urea hydrolysis in both experiments and analyzed the differ-

ences found between them. We assumed that the model ob-
tained from Experiment II gave the true effect of soil
water potential on urea hydrolysis because we maintained a
constant concentration at all soil water potential levels.
We also assumed that the effect of soil water potential is
independent of urea concentration. For a given soil water
potential in Experiment I we predicted its correspondent
relative rate (PRR) from the model developed in Experiment
II. We determined the concentration factor (CONFAC) to be
the difference between the observed relative rate of urea
hydrolysis in Experiment I (ORR), and PRR at a given soil
water potential :

$$CONFAC = ORR - PRR$$

The difference of absolute rate due to concentration
effect (DDC) was obtained by multiplying CONFAC by the
absolute rate measured in Experiment I (Reference absolute
rate or RAR) at approximately the same soil water poten-
tial at which the relative rate was 1 in Experiment II.
Then

$$DDC = CONFAC * RAR$$

The DDC values corresponded to a constant soil water
potential. To know how the absolute rate was affected by
concentration, we added the DDC value corresponding to
each concentration to the RAR

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$$RDC = DDC + RAR$$

where RDC is the rate calculated at each level of concentration once the effect of soil water potential has been accounted for (Figure 9). Smolan silt loam was not evaluated in this analysis because the soil water potential levels used in both experiments were different. The relationship found between RDC and urea-N concentration could be described using a modified Michaelis-Menten equation in which the rate is affected by uncompetitive inhibition as proposed by Singh and Nye (1984)

$$Rate = (V_{max} * Conc) / (Conc + K_m + (Conc^2 * K_i^{-1}))$$

where

V_{max} = maximum rate

Conc = urea-N concentration

K_m = Michaelis-Menten constant

K_i = inhibition constant

To check if this concentration effect was significant in general for all the limed soils in Experiment I, we adjusted a model for the relative rate with the soil water potential effect and the concentration effect

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DRR = SWP Effect + Conc Effect $R^2 = 0.77^*$

SWP Effect = (0.60*exp(0.27*SWP))

Conc Effect = (0.58*Conc)/(0.31+Conc+(Conc^2*2.67))

We compared the residual sum of squares of the model with the concentration effect and a model without it. The model without the concentration effect was

Relative Rate = 0.92 * exp (0.15 * SWP) $R^2 = 0.63^*$

The F value obtained was significant, therefore suggesting a significant concentration effect on the response of urease activity to soil water potential in Experiment I (Table 13). The relationship between relative rate of urea hydrolysis and soil water content could be also affected by this concentration effect.

The maximum rate of urea hydrolysis found for each soil in both experiments was related to the organic C and clay content through a correlation analysis using only the limed soils (Table 14). In Experiment I, a high and significant correlation was found between the rate of hydrolysis and organic C and clay content. A similar trend was

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observed in Experiment II, but the correlation coefficients were lower. The low correlation coefficients obtained compared with those reported by other authors (Zantua et al, 1977; Reynolds et al, 1985), could be due to the narrow range in organic C and clay content, and to the low number of soils used.

It will be important that future work, in this and other areas of study on urea hydrolysis, consider urea-N concentrations in soil solution and not urea-N concentrations on a soil mass basis. Our data suggest that urea hydrolysis occurs in solution. If urea is applied on a soil mass basis, a change in soil water content will change the urea-N concentration in the soil solution, thereby affecting the response of urea hydrolysis to any factor under study.

Table 1. Classification and some properties of the soils used in the study.

Soil	Classification	pH	Clay	Silt	Sand	Organic Carbon
			--------------------------g/kg--------------			
Captina silt loam	Fine-silty, Mixed, Mesic, Typic Fragiudults	6.4	90	690	220	4
Haynie very fine sandy loam	Coarse-silty, Mixed, Calcareous, Mesic, Typic Udifluvents	7.7	70	410	520	5
Kahola silt loam	Fine-silty, Mixed Mesic, Cumulic Hapludolls	5.5	17	810	20	14
Reading silt loam	Fine, Mixed,Mesic, Typic Argiudolls	6.0	20	740	60	10
Smolan silt loam	Fine, Montmorillonitic, Mesic, Pachic Argiustolls	6.2	26	700	40	12

Table 2. Amount of $Ca(OH)_2$ added and pH at the end of the seven days incubation period at 5°C.

Soil	Experiment I		Experiment II	
	$Ca(OH)_2$	pH	$Ca(OH)_2$	pH
	mmol OH⁻/kg		mmol OH⁻/kg	
Captina	18	8.1	18	8.3
Haynie	4	8.3	4	8.3
Kahola	110	8.2	110	8.2
Reading	50	8.1	50	8.2
Smolan	65	8.3	60	8.4

Table 3. Means of rate and relative rate of urea hydrolysis for the different levels of soil water potential in Experiment I.

Soil Water Potential	Soil Water Content	Rate[1]	Rate[2]	DRR[1]#	ARR[2]#
MPa	kg/kg	$mg\ kg^{-1}\ hr^{-1}$			
Captina					
0.12	0.13	5.35	5.57	0.78	0.70
0.22	0.10	5.80	6.62	0.85	0.83
0.40	0.08	6.18	7.66	0.90	0.96
0.77	0.06	6.84	7.96	1.00	1.00
1.51	0.04	5.62	5.49	0.82	0.69
11.30	0.02	0.38	0.62	0.06	0.08
Haynie					
0.11	0.13	11.18	9.24	0.83	0.91
0.17	0.11	9.34	9.33	0.70	0.92
0.33	0.08	10.38	9.79	0.78	0.96
0.46	0.07	13.38	10.15	1.00	1.00
3.39	0.03	6.53	7.22	0.49	0.71
12.63	0.02	1.00	0.90	0.08	0.09
Kahola at original pH					
0.13	0.22	10.62	10.12	1.00	1.00
0.23	0.18	10.28	9.78	0.97	0.97
0.66	0.13	9.96	8.01	0.94	0.79
1.59	0.10	10.03	5.84	0.94	0.58
2.49	0.09	8.68	5.65	0.82	0.56
10.24	0.06	7.15	1.40	0.67	0.14

1 Calculated by disappearance of urea.
2 Calculated by appearance of hydrolysis products.
Relative rate of urea hydrolysis.

Table 3. Continuation.

Kahola at pH 8.23

0.13	0.22	19.49	11.43	1.00	0.87
0.21	0.19	17.88	13.14	0.92	1.00
0.43	0.15	14.90	10.13	0.76	0.77
0.74	0.13	13.32	10.43	0.68	0.79
4.41	0.07	10.35	5.52	0.53	0.42
28.25	0.04	5.84	1.39	0.30	0.11

Reading at original pH

0.10	0.22	14.17	9.84	1.00	1.00
0.22	0.17	12.19	8.41	0.86	0.86
0.26	0.16	10.16	8.41	0.72	0.85
0.60	0.13	11.80	7.14	0.83	0.73
0.63	0.13	8.96	9.43	0.63	0.96
1.35	0.10	9.96	6.88	0.70	0.70

Reading at pH 8.13

0.12	0.21	21.74	17.54	1.00	1.00
0.29	0.16	21.04	16.68	0.97	0.95
0.65	0.12	18.85	14.53	0.87	0.83
0.87	0.11	19.47	13.30	0.90	0.76
63.04	0.03	8.92	0.92	0.41	0.05
82.58	0.02	7.78	0.84	0.36	0.05

Smolan

0.25	0.20	12.99	11.54	0.98	0.98
0.45	0.17	13.19	11.75	1.00	1.00
0.96	0.14	12.63	11.12	0.96	0.95
3.54	0.10	8.37	6.03	0.63	0.51
12.03	0.08	6.56	2.67	0.50	0.23
62.93	0.05	3.29	0.60	0.25	0.05

Table 4. Coefficients of models of the effect of soil water potential on relative rate of urea hydrolysis for each soil in Experiment I.

Soil		A	B	R^2
Captina	DRR	0.95	0.16	0.83
	ARR	0.91	0.16	0.81
Haynie	DRR	0.86	0.17	0.79
	ARR	0.99	0.14	0.93
Kahola at original pH				
	DRR	0.97	0.04	0.61
	ARR	0.99	0.26	0.96
Kahola at pH 8.23				
	DRR	0.83	0.05	0.64
	ARR	0.92	0.18	0.91
Reading at original pH				
	DRR	0.89	0.24	0.27
	ARR	0.95	0.23	0.33
Reading at pH 8.13				
	DRR	0.93	0.01	0.93
	ARR	1.05	0.36	0.99
Smolan	DRR	0.96	0.05	0.81
	ARR	1.05	0.16	0.97

General Model   Relative Rate = A*EXP(B*SWP)

Table 5. Test of null hypothesis for the effect of soil water potential on the relative rate of urea hydrolysis in Experiment I.

Source	Sum of Squares Residuals	df
Relative Rate by Disappearance (DRR)		
Pooled data(H_o)	3.975	124
Captina	0.305	16
Haynie	0.369	16
Kahola or.	0.131	16
Kahola 8.13	0.423	16
Reading or.	0.260	16
Reading 8.13	0.088	16
Smolan	0.291	16
Sum of soils(H_a)	1.867	112

SSdev# = 3.975-1.867 = 2.108   df= 124-112 = 12

Fc=(2108/12)/(1.867/112)=10.54   Fc > Ft (12,112)

Table 5. Continuation.

Relative Rate by appearance (ARR)

Pooled data(H_o)	1.292	124
Captina	0.320	16
Haynie	0.119	16
Kahola or.	0.067	16
Kahola 8.23	0.162	16
Reading or.	0.210	16
Reading 8.13	0.032	16
Smolan	0.070	16
Sum of soils(H_a)	0.980	112

SSdev# = 1.292-0.980 = 0.312   df = 124-112 = 12

Fc=(0.312/12)/(0.980/112)=2.97   Fc > Ft (12,112)

Sum of squares due to deviations of H_a from H_o.

Table 6. Means of N ammonified and N nitrified in the control
treatments at the different levels of soil water potential for
each soil in Experiment I.

Soil	Soil Water Potential	N Mineralized	N Nitrified
	MPa	-------- mg N kg^{-1}---------	
Captina	0.12	-2.5	1.3
	0.22	-3.3	1.0
	0.40	-2.2	1.2
	0.77	-2.4	0.8
	1.51	-2.8	0.4
	11.30	-3.6	-0.2
Haynie	0.11	-2.2	1.0
	0.17	-2.3	1.1
	0.33	-1.9	1.3
	0.46	-1.9	1.4
	3.39	-2.3	0.3
	12.63	-2.9	0.0
Kahola at original pH			
	0.13	-4.1	0.6
	0.23	-3.8	0.9
	0.65	-2.4	2.6
	1.59	-2.6	2.4
	2.49	-4.0	1.0
	10.24	-4.6	-0.2
Kahola at pH 8.23			
	0.13	0.2	1.9
	0.21	-0.8	2.6
	0.43	-0.8	2.1
	0.74	-1.6	2.0
	4.41	-2.7	0.2
	28.25	-3.3	0.0

Table 6. Continuation.

Reading at original pH

0.10	-2.6	0.8
0.22	-2.0	1.4
0.26	-1.9	1.6
0.60	-1.7	1.7
0.63	-2.2	1.6
1.35	-1.9	1.4

Reading at pH 8.13

0.12	0.6	3.1
0.29	-0.5	2.7
0.65	-1.4	1.6
0.87	-1.5	1.3
63.04	-3.1	-0.1
112.58	-3.1	-0.1

Smolan			
	0.25	-0.7	0.8
	0.45	-0.6	2.1
	0.96	-1.2	1.7
	3.54	-1.7	0.4
	12.03	-1.9	0.4
	62.93	-2.4	0.2

Table 7. Test of null hypothesis for effect of pH on the response of urea hydrolysis to soil water potential in Experiment I.

Source	Sum of Squares Residuals	df

Relative rate calculated by urea disappearance (DRR)

Kahola

Pooled data (H_o)	0.73	34
Kahola or.	0.13	16
Kahola 8.23	0.42	16
Sum individual models (H_a)	0.55	32

SSdev# = (0.73-0.55) = 0.18   df = 34-32 = 2

Fc=(0.18/2)/(0.55/32)=5.23   Fc > Ft (2,32)

Reading

Pooled data (H_o)	1.31	34
Reading or.	0.26	16
Reading 8.13	0.09	16
Sum individual models (H_a)	0.35	32

SSdev# = 1.31-0.35 = 0.96   df = 34-32 = 2

Fc = (0.96/2)/(0.35/32) = 43.88   Fc > Ft (2,32)

Table 7. Continuation.

Relative rate calculated by appearance (ARR)

Kahola

Pooled data (H_o)	0.25	34
Kahola or.	0.07	16
Kahola 8.23	0.16	16
Sum of individual models (H_a)	0.23	32

SSdev# = 0.25-0.23 = 0.02   df = 34-32 = 2

Fc = (0.02/2)/(0.23/32) = 1.33   Fc < Ft (2,32)

Reading

Pooled data (H_o)	0.26	34
Reading or.	0.21	16
Reading 8.13	0.03	16
Sum of individual models (H_a)	0.24	32

SSdev# = 0.26-0.24 = 0.02   df = 34-32 = 2

Fc = (0.02/2)/(0.24/32) = 1.33   Fc < Ft (2,32)

Sum of squares due to deviations.

Table 8. Means of Absolute and Relative Rate of Urea Hydrolysis for the different levels of Soil Water Potential in Experiment II.

Soil Water Potential	Soil water Content	Rate[1]	Rate[2]	DRR[1]#	ARR[2]#
MPa	kg/kg	mg kg^{-1} hour^{-1}			
Captina					
0.11	0.14	48.2	34.6	1.00	1.00
0.15	0.12	39.0	16.4	0.81	0.48
0.27	0.09	29.9	15.9	0.62	0.46
0.57	0.07	29.3	9.2	0.61	0.27
1.63	0.04	8.7	4.6	0.18	0.13
10.88	0.02	1.1	0.4	0.02	0.01
Haynie					
0.16	0.11	58.3	55.5	1.00	1.00
0.29	0.09	52.2	43.3	0.89	0.78
0.87	0.06	21.5	20.5	0.37	0.37
2.10	0.04	15.3	13.4	0.26	0.24
3.69	0.03	8.2	6.8	0.14	0.12
5.84	0.03	8.8	7.1	0.15	0.13
Kahola at original pH					
0.15	0.21	94.2	16.2	1.00	1.00
0.28	0.17	84.4	13.7	0.90	0.84
0.81	0.12	18.1	13.1	0.19	0.81
3.83	0.07	11.9	6.0	0.13	0.37
5.26	0.07	7.0	4.4	0.07	0.27
16.73	0.05	5.2	0.4	0.06	0.03
Kahola at pH 8.22					
0.19	0.20	91.3	52.5	1.00	1.00
0.28	0.17	92.1	46.6	1.00	0.89
0.76	0.13	50.2	24.2	0.54	0.46
0.79	0.12	55.0	29.7	0.60	0.60
1.97	0.09	30.5	16.3	0.33	0.31
5.21	0.07	25.7	11.3	0.28	0.21

1 Calculated by disappearance.
1 Calculated by appearance.
Relative rate of urea hydrolysis.

Table 8. Continuation.

Reading at pH original

0.10	0.21	42.8	32.4	1.00	1.00
0.15	0.19	39.5	31.3	0.92	0.96
0.31	0.16	38.9	30.7	0.91	0.95
0.61	0.13	31.1	25.2	0.73	0.78
1.36	0.10	20.8	17.3	0.49	0.53
5.24	0.07	10.8	6.9	0.25	0.21

Reading at pH 8.24

0.14	0.20	130.7	90.0	1.00	0.99
0.21	0.17	112.3	91.2	0.86	1.00
0.51	0.13	86.2	71.8	0.66	0.79
0.65	0.12	67.8	52.2	0.52	0.57
6.18	0.06	14.3	9.1	0.11	0.10
15.96	0.05	8.7	3.9	0.07	0.04

Smolan

0.11	0.24	59.7	41.8	1.00	1.00
0.33	0.18	48.9	35.6	0.82	0.85
0.71	0.15	39.8	31.3	0.67	0.75
0.96	0.14	35.6	26.8	0.60	0.64
3.97	0.10	22.8	13.9	0.38	0.33
4.82	0.10	12.7	9.8	0.21	0.23

Table 9. Test of null hypothesis for the effect of soil water potential on the relative rate of urea hydrolysis in Experiment II.

Source	Sum of Squares Residuals	df
Relative Rate by Disappearance (DRR)		
Pooled data(H_o)	2.65	124
Captina	0.31	16
Haynie	0.22	16
Kahola or.	0.16	16
Kahola 8.22	0.31	16
Reading or.	0.22	16
Reading 8.13	0.13	16
Smolan	0.14	16
Sum of soils(H_a)	1.50	112

SSdev# = 2.65-1.50 = 1.15   df = 124-112 = 12

Fc = (1.15/12)/(1.50/112) = 7.16   Fc > Ft (12,112)

Table 9. Continuation.

Relative Rate by Appearance (ARR)

Pooled data(H_o)	3.65	124
Captina	0.36	16
Haynie	0.16	16
Kahola or.	0.07	16
Kahola 8.22	0.26	16
Reading or.	0.16	16
Reading 8.13	0.13	16
Smolan	0.06	16
Sum of soils(H_a)	1.20	112

SSdev# = 3.65-1.20 = 2.45   df = 124-112 = 12

Fc = (2.45/12)/(1.20/112) = 19.05

Fc > Ft (12,112)

_____

Table 10. Coefficients of models of the effect of soil water potential on relative rate of urea hydrolysis for each soil in Experiment II.

Soil		A	B	R^2
Captina	DRR	1.00	1.06	0.86
	ARR	1.16	3.27	0.81
Haynie	DRR	1.12	0.89	0.90
	ARR	1.08	0.94	0.92
Kahola at original pH	DRR	1.48	2.18	0.94
	ARR	0.98	0.25	0.97
Kahola at pH 8.23	DRR	1.10	0.66	0.80
	ARR	1.09	0.79	0.83
Reading at pH original	DRR	0.98	0.39	0.84
	ARR	1.02	0.39	0.90
Reading at pH 8.13	DRR	1.14	1.17	0.94
	ARR	1.17	0.93	0.96
Smolan	DRR	0.91	0.29	0.89
	ARR	0.96	0.30	0.96

Table 11. Means of N ammonified and N nitrified in the control treatments at the different levels of soil water potential in Experiment II.

Soil	Soil Water Potential	N Mineralized	N Nitrified
	MPa	---------- mg N kg^{-1} ---------	
Captina	0.11	-2.47	1.68
	0.15	-2.47	1.51
	0.27	-2.17	1.79
	0.57	-2.89	1.18
	1.63	-2.90	1.68
	10.88	-3.49	0.05
Haynie	0.16	-2.92	1.82
	0.29	-3.23	1.59
	0.87	-3.08	1.62
	2.10	-3.57	0.94
	3.69	-3.73	0.20
	5.84	-3.48	0.40
Kahola at original pH			
	0.15	-5.93	0.82
	0.28	-5.75	1.03
	0.81	-5.90	1.02
	3.83	-6.18	0.03
	5.26	-6.15	0.07
	16.73	-6.27	-0.10
Kahola at pH 8.22			
	0.19	-0.84	1.34
	0.28	-1.61	1.44
	0.76	-2.16	1.57
	0.79	-2.51	1.22
	1.97	-4.26	0.24
	5.21	-5.46	-0.13

Table 11. Continuation.

Reading at original pH			
	0.10	-5.31	0.97
	0.15	-4.69	1.48
	0.31	-4.49	1.52
	0.62	-4.42	1.47
	1.36	-4.96	1.23
	5.24	-5.29	0.22
Reading at pH 8.24			
	0.14	-3.66	2.16
	0.21	-3.74	2.26
	0.51	-3.43	2.34
	0.65	-3.16	2.14
	6.18	-5.23	-0.52
	15.96	-5.98	-0.79
Smolan	0.11	-2.94	2.48
	0.33	-4.50	1.10
	0.71	-3.20	1.42
	0.96	-4.27	0.47
	3.97	-4.14	-0.30
	4.82	-5.39	-0.63

Table 12. Test of null hypothesis for the effect of pH on the response of urea hydrolysis to soil water potential in Experiment II.

Source	Sum of squares residuals	df
Relative Rate by Disappearance (DRR)		
Kahola		
Pooled data (H_o)	0.84	34
Kahola or.	0.16	16
Kahola 8.22	0.31	16
Sum of individual models (H_a)	0.47	32

SSdev# = 0.84-0.47 = 0.37   df = 34-32 = 2

Fc = (0.37/0.02)/(0.47/32) = 12.6   Fc > Ft (2,32)

Reading		
Pooled data (H_o)	0.52	34
Reading or.	0.22	16
Reading 8.24	0.13	16
Sum of individual models (H_a)	0.35	32

SS dev# = 0.52-0.35 = 0.17   df = 34-32 = 2

Fc = (0.17/2)/(0.35/32) = 7.77   Fc > Ft (2,32)

Table 12. Continuation.

Relative Rate by Appearance (ARR)

Kahola

Pooled data (H_o)	0.65	34
Kahola or.	0.07	16
Kahola 8.22	0.26	16
Sum of individual models (H_a)	0.33	32

SSdev# = 0.65-0.29 = 0.32   df = 34-32 = 2

Fc = (0.32/2)/(0.33/32) = 15.5   Fc > Ft (2,32)

Reading

Pooled data (H_o)	0.37	34
Reading or.	0.16	16
Reading 8.24	0.13	16
Sum of individual models (H_a)	0.29	32

SSdev# = 0.37-0.29 = 0.08   df = 34-32 = 2

Fc = (0.08/2)/(0.29/32) = 4.41   Fc > Ft (2,32)

SSdev = Sum of squares due to deviations.

Table 13. Comparison between models with and without concentration effect on the relative rate of urea hydrolysis in Experiment I.

Hypothesis	df_{res}	SS_{res}	MS_{res}	$F^{[1]}$
$Ho^{[2]}$	70	2.280	0.033	
$Ha^{[3]}$	67	1.423	0.021	13.6*

[1] $F = (SS_{resHo} - SS_{resHa} / df_{Ho} - df_{Ha}) / MS_{resHa}$

[2] Model without concentration effect

[3] Model with concentration effect

Table 14. Correlation between the maximum rate of urea hydrolysis, organic carbon and clay content.

Experiment I	Rate[1]	Rate[2]	Organic C	Clay
Rate[1]	1			
Rate[2]	0.92***	1		
Organic C	0.65***	0.54***	1	
Clay	0.46***	0.60***	0.79***	1

Experiment II	Rate[1]	Rate[2]	Organic C	Clay
Rate[1]	1			
Rate[2]	0.95***	1		
Organic C	0.36***	0.20		
Clay	0.33**	0.22*	0.79***	1

*, **, *** Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.
1 Calculated by disappearance of urea.
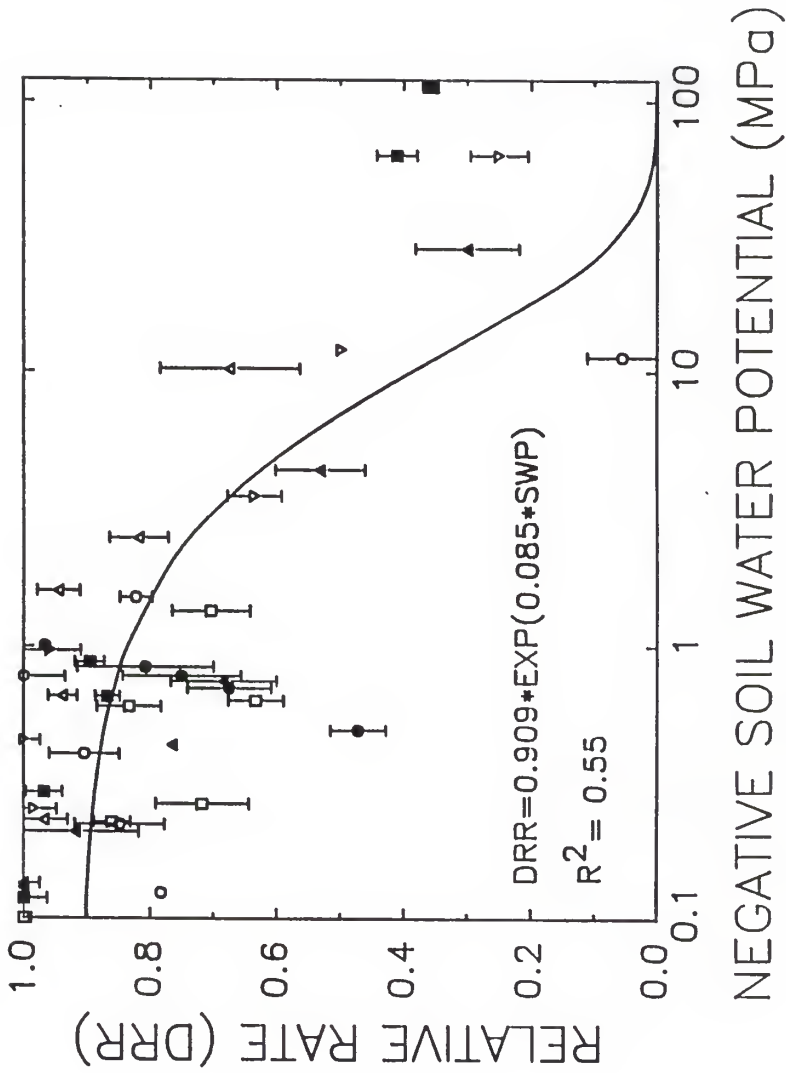2 Calculated by appearance of hydrolysis products.

Fig.1 Relative rate of urea hydrolysis (DRR) versus soil water potential in Experiment I

Fig.2 Relative rate of urea hydrolysis (ARR)
versus soil water potential in
Experiment I

Fig.3 Relative rate of urea hydrolysis (DRR)
versus soil water content in
Experiment I

Fig.4 Relative rate of urea hydrolysis (ARR)
versus soil water content in
Experiment I

ARR=1.598+(0.882*LOG SWC)

R^2=0.59

Fig.5 Relative rate of urea hydrolysis (DRR)
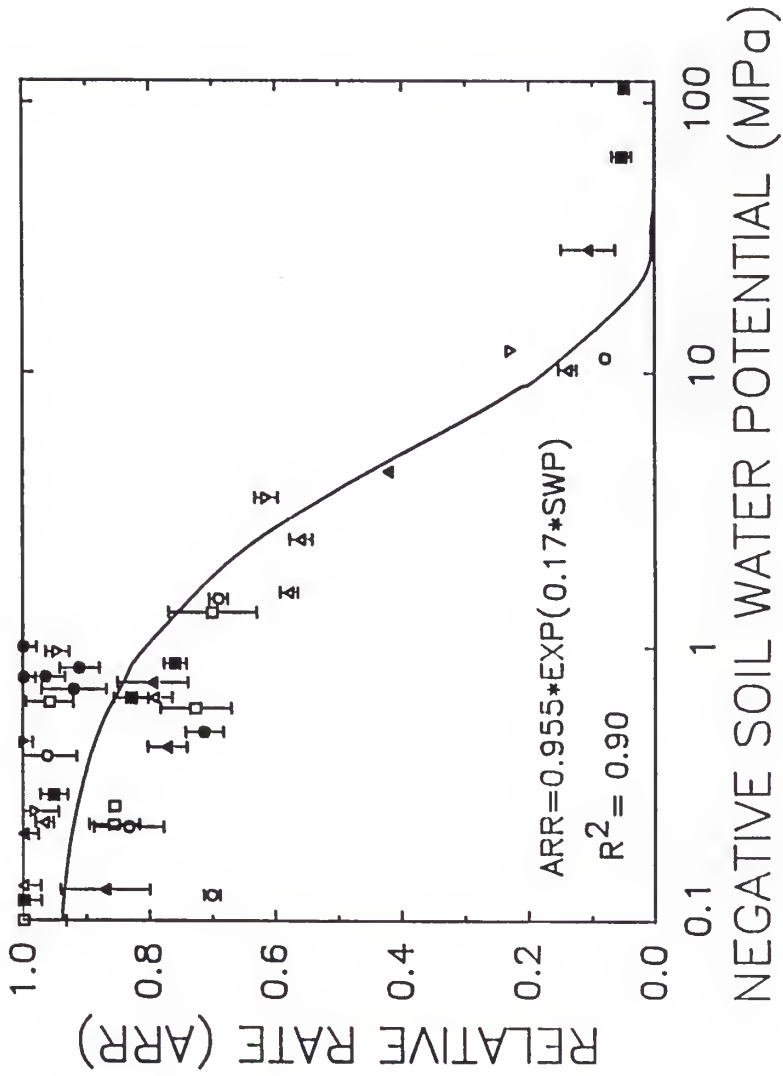versus soil water potential in
Experiment II

Fig.6 Relative rate of urea hydrolysis (ARR)
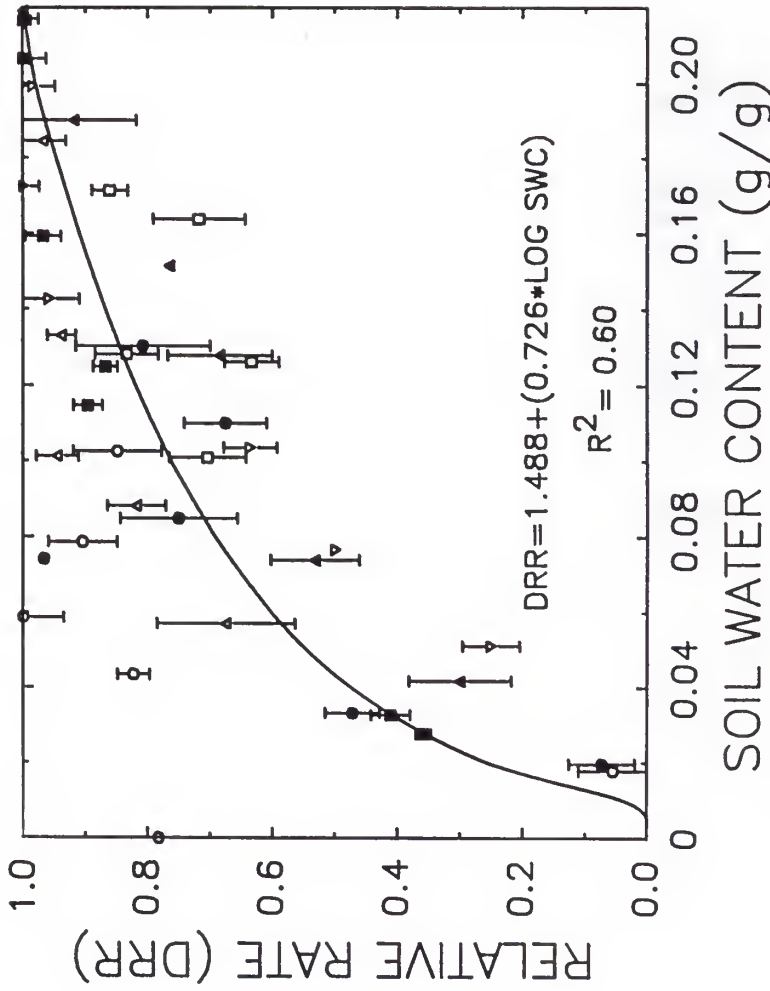versus soil water potential in
Experiment II

Fig.7 Relative rate of urea hydrolysis (DRR)
versus soil water content in
Experiment II

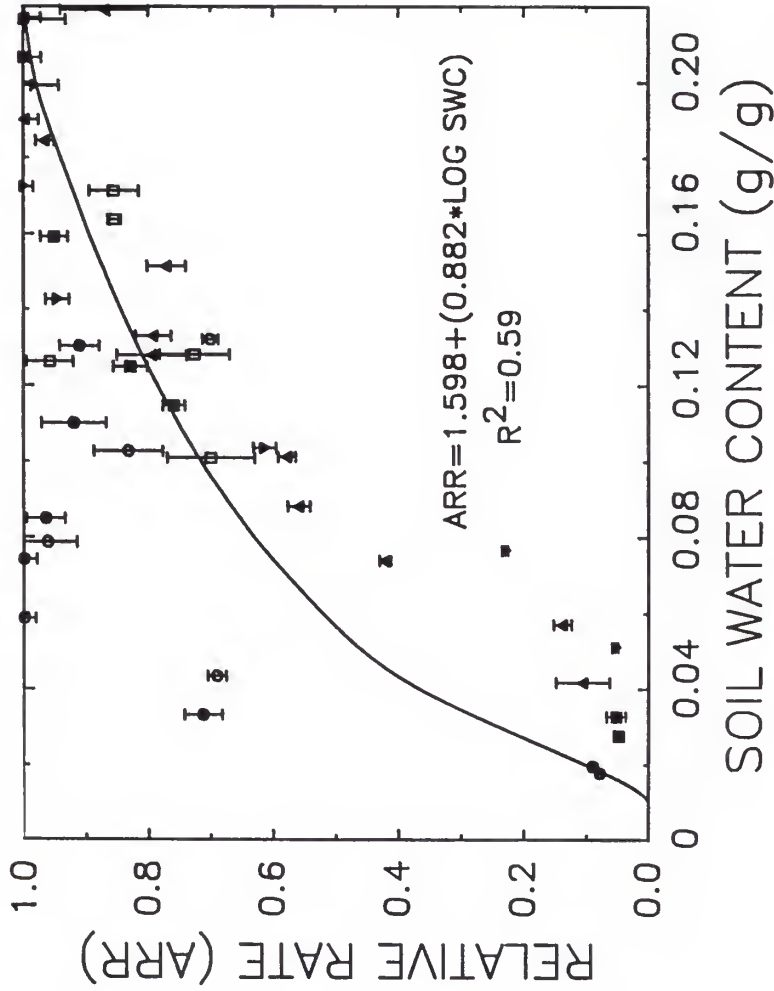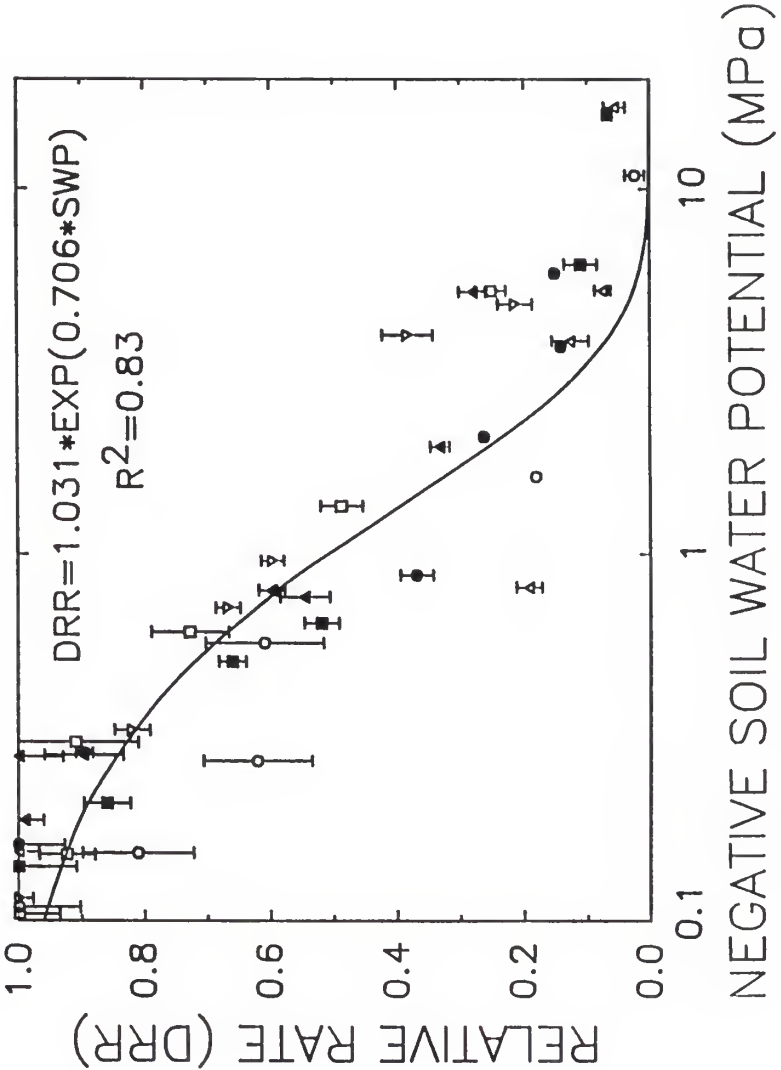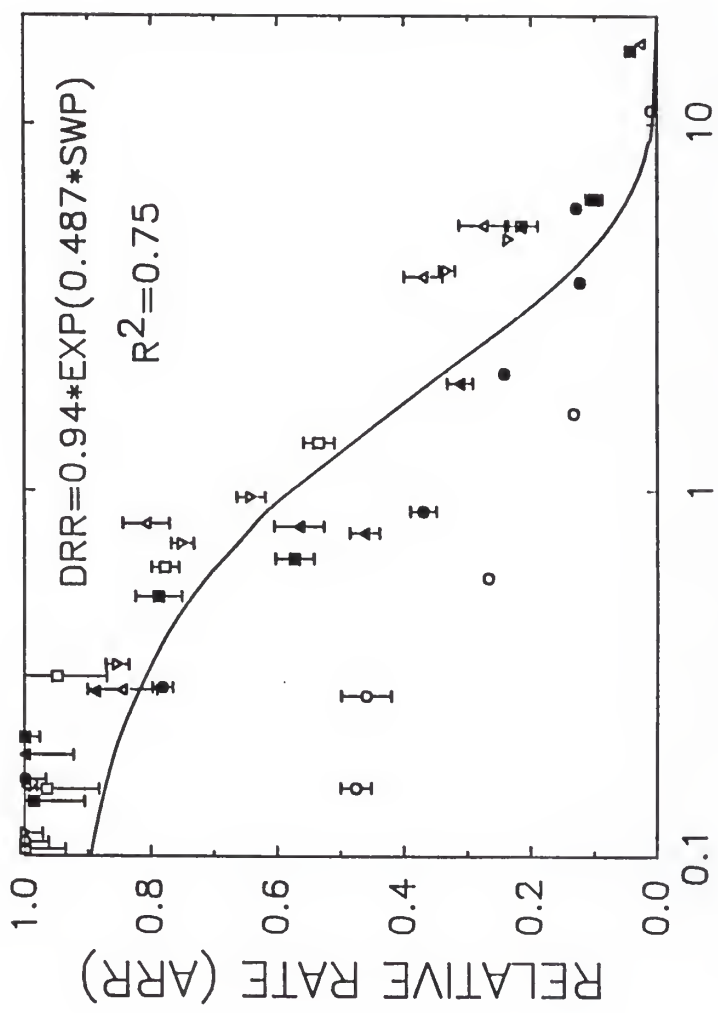DRR=-0.029+(5.081*SWC)

R^2=0.70
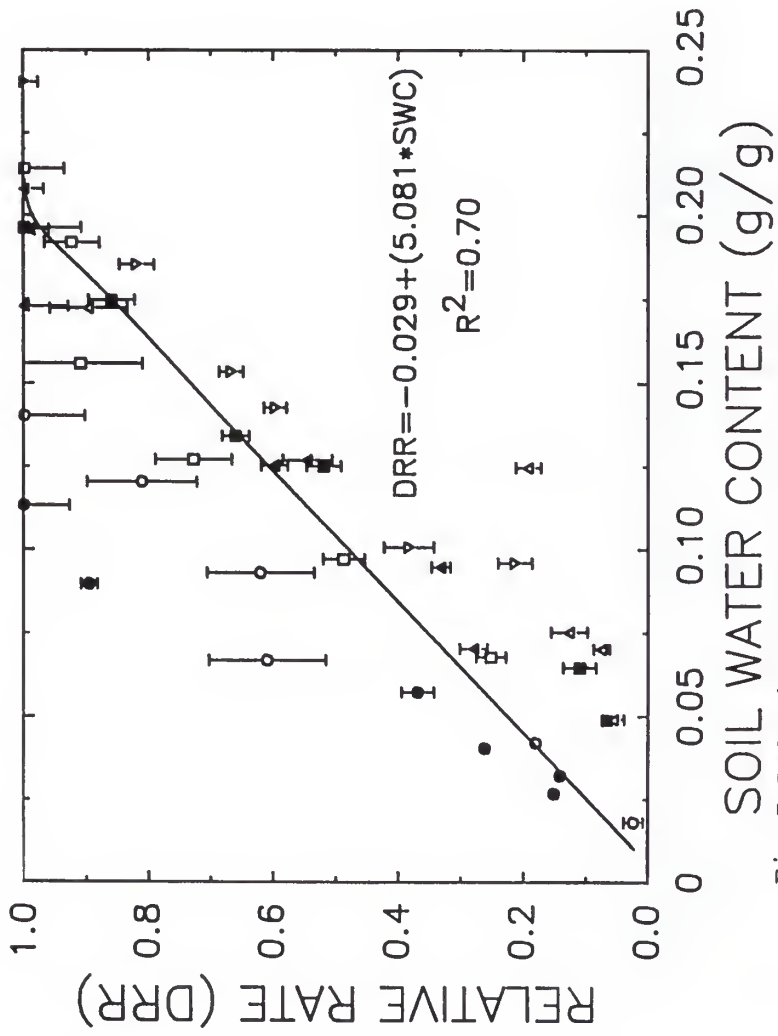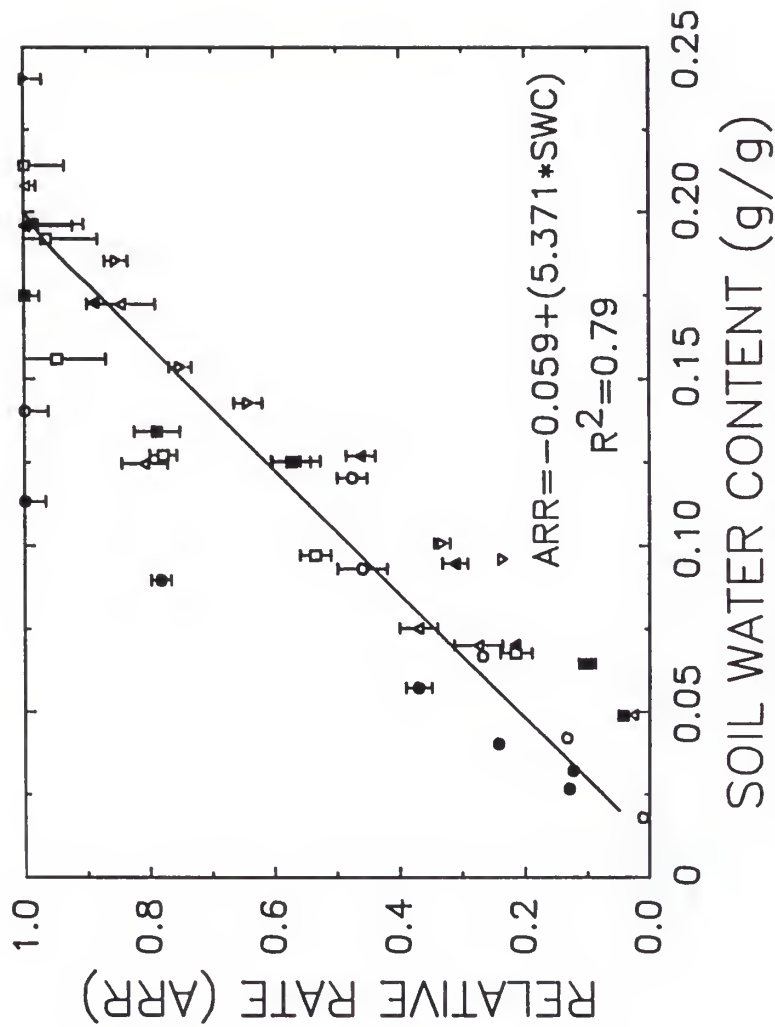
Fig.8 Relative rate of urea hydrolysis (ARR)
versus soil water content in
Experiment II
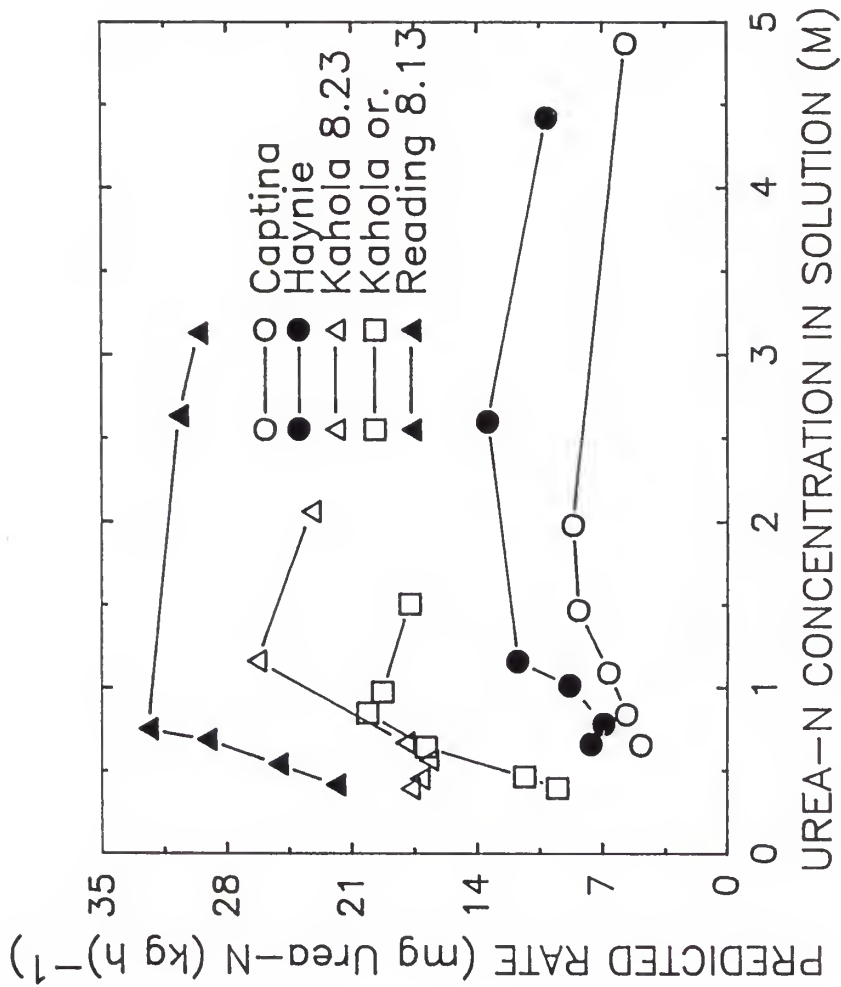
Fig.9 Predicted rate of urea hydrolysis versus urea-N concentration in solution at a same soil water potential in Experiment I

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APPENDIX

Table A1. Means of initial NH_4^+-N and NO_3^--N, and final NH_4^+-N, NO_3^--N, urea-N, and pH for the levels of soil water potential in Experiment I.

Soil water Potential	Initial NH_4^+-N	Initial NO_3^--N	Final NH_4^+-N	Final NO_3^--N	Final Urea-N	Final pH
MPa	----------- mg N (kg soil)$^{-1}$ ------------					
Captina						
0.12	5.0	1.9	135	3.2	1071	8.3
0.22	5.0	1.9	160	2.6	1060	8.3
0.40	5.0	1.9	185	2.7	1051	8.3
0.77	5.0	1.9	193	2.2	1035	8.4
1.51	5.0	1.9	134	1.8	1065	8.4
11.29	5.0	1.9	16	1.7	1200	8.0
Haynie						
0.11	3.6	1.3	222	2.0	931	8.6
0.17	3.6	1.3	225	1.6	975	8.6
0.33	3.6	1.3	235	2.2	950	8.6
0.46	3.6	1.3	244	1.7	878	8.7
3.39	3.6	1.3	175	1.0	1043	8.7
12.63	3.6	1.3	22	1.1	1177	8.4
Kahola at original pH						
0.13	5.4	1.6	238	7.1	945	6.1
0.23	5.4	1.6	232	5.9	953	5.9
0.65	5.4	1.6	191	5.6	960	5.8
1.59	5.4	1.6	140	4.3	959	5.7
2.49	5.4	1.6	135	3.3	991	5.7
10.24	5.4	1.6	34	1.4	1028	5.3
Kahola at pH 8.23						
0.13	5.6	1.7	280	1.7	732	8.2
0.21	5.6	1.7	320	1.8	770	8.2
0.43	5.6	1.7	247	1.9	842	8.1
0.74	5.6	1.7	254	1.9	880	8.0
4.41	5.6	1.7	135	1.4	951	8.0
28.25	5.6	1.7	35	1.4	1059	7.4

Table A1. Continuation.

Reading at pH original						
0.10	4.1	1.2	234	4.6	860	7.1
0.22	4.1	1.2	200	5.0	907	7.1
0.26	4.1	1.2	200	5.0	956	7.1
0.60	4.1	1.2	170	3.6	916	6.9
0.63	4.1	1.2	225	3.5	985	7.0
1.35	4.1	1.2	165	2.3	960	6.8
Reading at pH 8.13						
0.12	5.2	2.3	425	4.1	678	8.1
0.29	5.2	2.3	403	4.1	695	8.2
0.65	5.2	2.3	351	3.2	747	8.2
0.87	5.2	2.3	322	2.8	732	8.2
63.04	5.2	2.3	24	2.2	985	7.9
112.58	5.2	2.3	22	2.2	1013	7.9
Smolan						
0.25	5.0	2.7	279	4.9	888	8.0
0.45	5.0	2.7	284	4.9	883	8.0
0.96	5.0	2.7	269	4.2	896	8.1
3.54	5.0	2.7	147	3.3	999	8.0
12.03	5.0	2.7	66	3.3	1042	8.0
62.93	5.0	2.7	16	3.3	1121	7.9

Table A2. Means of initial NH_4^+-N and NO_3^--N, and final NH_4^+-N, NO_3^--N, urea-N, and pH for the levels of soil water potential in Experiment II.

Soil Water Potential	Initial NH_4^+-N	Initial NO_3^--N	Final NH_4^+-N	Final NO_3^--N	Final Urea-N	Final pH
MPa	-----------	mg N (kg soil)$^{-1}$		-----------		
Captina						
0.11	4.6	1.8	833	1.8	4446	8.8
0.15	4.6	1.8	396	1.8	3870	8.8
0.27	4.6	1.8	383	2.0	3000	8.7
0.57	4.6	1.8	233	1.9	1956	8.5
1.63	4.6	1.8	111	1.7	1463	8.4
10.88	4.6	1.8	10	1.8	690	8.1
Haynie						
0.16	5.2	1.3	1333	1.7	3126	9.0
0.29	5.2	1.3	1041	1.8	2326	9.0
0.87	5.2	1.3	493	1.9	1768	8.9
2.10	5.2	1.3	322	1.7	1236	8.8
3.69	5.2	1.3	164	1.2	1078	8.8
5.84	5.2	1.3	172	1.4	846	8.8
Kahola at original pH						
0.15	7.2	0.8	388	1.8	6050	7.0
0.28	7.2	0.8	328	2.4	4860	6.9
0.81	7.2	0.8	314	1.8	4546	6.7
3.83	7.2	0.8	144	0.9	2796	6.0
5.26	7.2	0.8	107	0.8	2628	5.9
16.73	7.2	0.8	11	0.7	1829	5.5
Kahola at pH 8.22						
0.19	8.2	1.1	1268	1.3	5636	8.4
0.28	8.2	1.1	1125	1.3	4696	8.5
0.76	8.2	1.1	587	1.2	3866	8.4
0.80	8.2	1.1	717	1.2	3686	8.3
1.97	8.2	1.1	395	1.3	3048	8.2
5.21	8.2	1.1	273	1.2	2186	8.3

Table A2. Continuation.

Reading at original pH

0.10	6.6	0.5	778	1.0	7533	8.0
0.15	6.6	0.5	751	1.2	6720	8.0
0.31	6.6	0.5	738	1.3	5296	7.9
0.62	6.6	0.5	605	1.0	4333	7.9
1.36	6.6	0.5	415	1.4	3380	7.6
5.24	6.6	0.5	167	0.7	2446	6.9

Reading at pH 8.24

0.14	7.2	4.2	2163	4.4	4713	8.8
0.21	7.2	4.2	2193	4.3	4290	8.8
0.51	7.2	4.2	1726	4.2	3296	8.7
0.65	7.2	4.2	1256	3.9	3373	8.6
6.18	7.2	4.2	221	3.7	2231	8.3
15.96	7.2	4.2	95	3.5	1736	8.1

Smolan

0.11	7.7	6.1	1008	6.1	8179	8.3
0.33	7.7	6.1	858	6.3	6230	8.4
0.71	7.7	6.1	756	6.1	5176	8.3
0.96	7.7	6.1	646	6.0	4850	8.2
3.97	7.7	6.1	336	5.8	3475	8.3
4.82	7.7	6.1	238	5.9	3526	8.3

EFFECTS OF SOIL WATER EVAPORATION AND POTENTIAL

ON UREA TRANSFORMATIONS IN SOIL

by

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ABSTRACT

Urea has become the world's leading nitrogen fertilizer
material. In order to use urea efficiently, it is impor-
tant to know how soil, management, and environmental
factors affect its transformations in soil.

We conducted a study to evaluate the effect of soil
water evaporation on ammonia volatilization from surface-
applied urea and on the movement of urea and its hydroly-
sis products. We used a laboratory apparatus that allowed
to get different soil water evaporation rates from soil
columns by passing air at different levels of relative
humidity. In spite of the large difference in soil water
evaporation, there were no significant differences between
treatments. Urea and its hydrolysis products concentrated
at the soil surface due to the upward soil water flux in
the dry air treatment. In the wet air treatment, urea
diffused deeper before hydrolysis occurred. The results of
this research were not conclusive and future work with a
better control of variables such as soil water potential
is suggested.

In a second study, we evaluated the effect of soil
water potential on urea hydrolysis through two different
experiments. In Experiment I we used a constant concentra-
tion of urea-N on a soil mass basis, and in Experiment II
we used a constant concentration on a soil solution basis.

Five soils limed to pH about 8.2 and two of them at their original pH were used in the study. Models were fitted for each soil describing the relationship between relative rate of urea hydrolysis and soil water potential in both experiments. General models grouping data from all soils were also fitted, however statistical analysis showed that the relationship depended on the soil under study. The absolute rate of urea hydrolysis was higher in the limed soils than in the soils at the original pH. In both experiments a N deficit was observed which could be due to ammonia volatilization or ammonium fixation during the incubation period. Differences in relative rate of urea hydrolysis between both experiments suggested that there was a confounding of urea-N concentration on the response of urea hydrolysis to soil water potential in Experiment I. A modified Michaelis-Menten equation in which the rate is affected by uncompetitive inhibition accounted for this effect.