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Volatilization losses of surface-applied urea nitrogen from Vertisols in the Indian semi-arid tropics
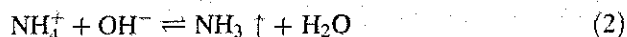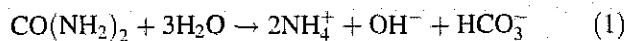
Abstract The N loss from Vertisols was estimated by measuring the loss of ^{15}N-labelled urea N under conditions that promote NH$_3$ volatilization. Urea granules were placed on the top of 150-mm deep soil columns (Vertisols) collected from three sites with a range in pH, electrical conductivity, and cation exchange capacity. There were two contrasting moisture treatments, one near field capacity (wet) and another with intermittent wetting of the soil surface before allowing the columns to dry (moist-dry). The results indicated that losses were influenced markedly by pH and moisture treatment, being 29.5, 33.5, and 33% from the wet soils and 37, 42, and 40.5% from the moist-dry soils with pH values of 7.7, 8.2, and 9.3, respectively. These observations clearly indicate that broadcasting of urea on the surface of Vertisols may cause substantial N losses.

Key words Vertisol · pH · Cation exchange capacity Moisture · Urea · ^{15}N · Nitrogen losses · Ammonia volatilization

Introduction

Because of the advantages associated with urea, it is the worldwide dominant source of solid N fertilizer (Hignett 1979). However, it has some inherent disadvantages, also. When urea is applied to soil it undergoes different transformations. In the presence of a higher soil pH (>7.0),

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NH$_4^+$ formed from urea (Eq. 1) is deprotonized to form NH$_3$ gas (Eq. 2):

$$CO(NH_2)_2 + 3H_2O \rightarrow 2NH_4^+ + OH^- + HCO_3^- \qquad (1)$$

$$NH_4^+ + OH^- \rightleftharpoons NH_3 \uparrow + H_2O \qquad (2)$$

This reaction may account for the loss of significant amounts of NH$_3$, especially when urea fertilizer is applied to the surface of agricultural soils in arid and semi-arid regions (Terman 1979). Several soil and climatic factors influence NH$_3$ volatilization from soil (Freney et al. 1983). Increased losses are associated with greater initial soil alkalinity, higher temperatures, and soil drying, during or soon after urea hydrolysis (Simpson 1968). NH$_3$ volatilization of the surface-applied urea may be particularly large following a light rainfall (<15 mm) that is sufficient to moisten the soil but not enough to leach the urea to any substantial depth, most likely because of an increase in the rate of urea hydrolysis (Mahendrappa and Ogden 1973; Craig and Wollum 1982), resulting in a higher pH and a greatly increased concentration of NH$_4^+$ at the soil surface.

A higher soil pH, high temperatures, and frequent light rainfalls in the early monsoon period (June) normally prevail in the Vertisols of the semi-arid tropics in this part of India. When urea is applied on the surface of these soils without incorporating it into the soil, either as a separate operation before dry-seeding or as a combined operation with dry-seeding (Kanwar et al. 1978; El-Swaify et al. 1985), losses of N may be quite significant. The present study was undertaken to assess the magnitude of N losses when urea was applied evenly as granules on the surface of three Vertisols varying in soil pH, electrical conductivity, and cation exchange capacity, with two contrasting moisture treatments. This study was conducted with ^{15}N-labelled urea, and losses were calculated from the ^{15}N recovered from the fertilized soils.

Materials and methods

Soils

The soils used were surface (0–15 cm) samples of three heavy-textured Vertisols differing in pH, electrical conductivity, and cation exchange capacity from the International Crops Research Institute for the Semi-Arid Tropics (ICRISAT) Center farm located about 25 km north-west of Hyderabad, India (17.5°N, 78.5°E, altitude 545 m). The samples were air-dried and ground to pass a 2-mm screen for laboratory analysis. For organic-C analysis, soil samples were ground to pass a 0.5-mm sieve.

For soil analysis, pH was determined by a glass electrode, organic C by dichromate oxidation (Walkley and Black 1934), and cation exchange capacity by 1 N sodium acetate solution (pH 8.2) as described by Jackson (1967). NH_4^+ and NO_3^- contents were determined with MgO and Devardas alloy as described by Bremner (1965), and particle-size distribution was determined after destruction of organic matter by the hydrometer method (Day 1965). Some characteristics of the Vertisols are given in Table 1.

Columns

In the laboratory, columns of soil (150 mm depth and 71 mm internal diameter) were prepared by packing the sieved soil (0.5 kg) into polyvinyl chloride (PVC) tubing. The base of each column was covered by thin plastic sheet and sealed with araldite (Hindustan Ciba-Geigy Limited, Bombay, India). The walls of the columns were covered with black insulation tape to minimize the effect of horizontal light penetration.

Treatment

^{15}N-labelled (5.023% atom excess) urea as solid granules was placed onto the surface of the soils. The quantities of fertilizer N applied to these soils are shown in Tables 2 and 3. The initial target was to apply urea at a rate of 200 µg N g^{-1} soil. At this rate 217.4 mg urea (46%N) was needed for each column of soil. However, as the granules of urea were not of uniform weight there was a practical difficulty in obtaining exactly the same quantity each time. Even if time had been taken to weigh the granules some error would have been unavoidable because urea absorbs atmospheric moisture very quickly. To minimize these difficulties and/or errors, the N was applied at different rates. After the application, a measured quantity of water was sprinkled on the soil to provide two moisture treatments: one at field capacity (wet) and another that moistened the soil to a depth of 15 mm (moist-dry). The wet treatment was applied only once but the moist-dry treatment was applied for a second time 48 h later. All soil columns were placed outside the laboratory to provide a field environment. There were three replicates. Average minimum and maximum temperatures during the experimental period were 24°C and 39°C, respectively.

Table 1 Some characteristics of the soils used. Values are means of two independent analyses and the two values did not differ by more than 5%. *EC* electrical conductivity, *CEC* cation exchange capacity

Property	Vertisol 1	Vertisol 2	Vertisol 3
pH (1:2 soil:H$_2$O)	7.7	8.2	9.3
EC (dS m^{-1}); 1:2 soil:H$_2$O)	0.1	0.2	1.3
CEC [cmol (p$^+$) kg^{-1}]	34	37	19
Organic C (%)	0.55	0.43	0.54
Total N (mg kg^{-1})	750	562	654
NH$_4^+$ (mg kg^{-1})	6.3	4.2	2.1
NO$_3^-$ (mg kg^{-1})	5.3	0	2.2

Sampling

Soil samples were taken twice, immediately after the fertilizer application on the air-dried soil and again at the end of 7 days. Although the experiment could have benefited from an increased number of samples taken over a longer time, it was designed to simulate local conditions. In this region after dry-seeding in early June, the rainfall generally remains light. Moreover, we expected a clear pattern of N losses to appear within a week after the urea application, as maximal N losses from NH$_3$ volatilization have been reported to occur in the first 7–10 days (Whitehead and Raistrick 1990; Fan and Mackenzie 1993; Al-Kanani et al. 1994).

The soil samples were analysed for total Kjeldahl N (Bremner and Mulvaney 1982), and subsequently for ^{15}N content with an optical Emission ^{15}N Analyzer (JASCO, Japan). ^{15}N recovery from soil was calculated using the following approaches:

$$\text{N derived from fertilizer (Ndff)} = \frac{^{15}\text{N excess (sample)}}{^{15}\text{N excess (fertilizer)}}$$

$$\text{Recovery of fertilizer N} = \text{total soil N} \times \text{Ndff}$$

Per cent N recovered from soil (tracer method)

$$= \frac{\text{fertilizer N recovered}}{\text{rate of fertilizer N application}} \times 100$$

Per cent N recovered form soil (by difference method)

$$= \frac{\text{N recovered from treated sample} - \text{N recovered from control sample}}{\text{rate of fertilizer N application}} \times 100$$

$$\text{Fertilizer N losses} = \text{fertilizer N applied} - \text{fertilizer N recovered}$$

Results and discussion

The N recovery immediately after fertilizer application was measured in air-dried soils (Table 2) and the results showed complete recovery of fertilizer N in all the soils. However, the percentage of N derived from fertilizer was highest in Vertisol 2 (24%) and lowest in Vertisol 1 (19%). These differences were mainly due to the variable dilution of added ^{15}N because of variations in the soil total-N content (Table 1). Soil with a higher content of N gave a lower percentage of N derived from fertilizer and vice versa.

The recovery of added N after 7 days was markedly reduced in all soils and this was even more marked when the ^{15}N technique was used (Table 3). In the wet treatments, 70.5, 66.5, and 67.1% ^{15}N urea N was recovered from Vertisols 1, 2, and 3, respectively. Thus N losses from these soils were substantial. In the moist-dry treatment the extent of N loss was still higher, at 37, 42, and 40% from Vertisols 1, 2, and 3, respectively (Table 3). This indicates that a moist-dry soil after the application of urea allows greater N losses than a wet soil. Although we did not measure N losses directly we assume that the loss was mainly due to NH$_3$ volatilization, because there was no leaching and the moisture level was not high enough to create anaerobic conditions for denitrification. Earlier studies at the ICRISAT Center have indicated that urea hydrolysis is rapid in these soils. Almost all the urea was hydrolysed within 24 h of appliction, at a soil moisture content near field capacity and soil temperatures of 27–37°C (Sahrawat

Table 2 Recovery of added fertilizer N from Vertisols immediately after fertilizer application. Soils 1, 2, and 3 represent Vertisol 1 (pH 7.7), Vertisol 2 (pH 8.2), and Vertisol 3 (pH 9.3). *Ndff* N derived from fertilizer

Added N (μg g^{-1})	Total N recovery (μg g^{-1})	Ndff (%)	Fertilizer N recovery (μg g^{-1})		Fertilizer N recovery (%)	
			Difference method	^{15}N method	Difference method	^{15}N method
Soil 1						
0	774	–	–	–	–	–
186	967	19.4	193.0	188.0	104.0	101.0
Soil 2						
0	564	–	–	–	–	–
182	763	24.3	187.5	185.6	103.0	102.0
Soil 3						
0	667	–	–	–	–	–
182	851	22.0	183.8	185.6	101.0	102.0
SEM	±57.24	±1.41	±2.67	±0.8	±0.88	±0.33

Table 3 Recovery of fertilizer N from Vertisols 7 days after application. For further explanations, see Table 2

Added N (μg g^{-1})	Total N recovery (μg g^{-1})	Ndff (%)	Fertilizer N recovery (μg g^{-1})		Fertilizer N recovery (%)	
			Difference method	^{15}N method	Difference method	^{15}N method
Field capacity (wet)						
Soil 1						
0	728	–	–	–	–	–
189.5	880	15.2	152.5	133.6	80.5	70.5
Soil 2						
0	595	–	–	–	–	–
191.4	736	17.3	140.7	127.3	73.5	66.5
Soil 3						
0	655	–	–	–	–	–
184.8	803	15.4	147.5	124.0	79.8	67.1
SEM	±41.47	±0.67	±3.42	±2.82	±2.22	±1.24
Moist-dry						
Soil 1						
0	786	–	–	–	–	–
198.2	938	13.3	151.6	124.9	76.5	63.0
Soil 2						
0	572	–	–	–	–	–
186.5	710	15.2	138.4	108.2	74.2	58.0
Soil 3						
0	677	–	–	–	–	–
177.8	797	13.3	120.9	105.8	68.0	59.5
SEM±	±50.75	±0.63	±8.89	±6.00	±2.54	±1.48

1984). Similar phenomena have been observed more recently (Jayakumar 1992) in a field study on Vertisols.

Xu et al. (1993) have observed a good correlation between temperature and urea hydrolysis. They concluded that the rate of urea hydrolysis in soil increased with increasing temperature from 5 to 45°C. Due to the rapid hydrolysis of urea, the concentration of NH_4^+ increased on the soil surface and the alkaline pH of the soil facilitated the volatilization of NH_3. With a drier soil surface and higher diurnal temperatures the losses increased (Ernst and Massey 1960). As the temperature was quite high during the present experiment, the surface of the wet soils lost moisture more rapidly and as there was no significant reservoir of moisture in the water-limited soil (0.5 kg) it was dry after 3 days. If the soil surface dries and is not rewetted by dew or light rainfall, the NH_3 loss is reduced because of insufficient moisture for the necessary bio-

chemical and chemical reactions (Bouwmeester et al. 1985; Ferguson and Kissel 1986; McInnes et al. 1986). This indicates that the loss of N may have been greatest during the first 2–3 days (about 30–34%; Table 3). Because of the second addition of water in the moist-dry treatments, the soil surface remained moist for a longer time than in the wet treatment. This might have promoted fluxes of NH_3 for a prolonged time and produced higher losses of N (about 40%).

Several groups have reported higher N losses. The magnitude of NH_3 losses under laboratory conditions commonly range from 20 to 60% of the applied N, but have reached 90% when N is applied to the surface of sandy soils with a very low buffering capacity (Fenn and Hossner 1985). However, smaller losses have been reported under field conditions, ranging from 0 to 50% of the applied N (Hargrove 1988).

These Vertisols appear to have a buffering capacity with an initial pH of 7.7–9.3, effectively preventing a decrease in pH and allowing appreciable NH_3 volatilization to occur over a longer period of time (Avnimelech and Lahar 1977; Vlek and Stumpe 1978). Otherwise, H^+ resulting from the NH_3 loss and nitrification process could have lowered the soil pH at microsites and reduced the potential for NH_3 volatilization (Vlek and Stumpe 1978; Fan and Mackenzie 1993). From the present results, a pH value of 7.7 in Vertisols seems high enough to cause a significant loss of N through NH_3 volatilization; there was no added effect beyond pH 7.7 in either of the moisture treatments (Table 3).

Cation exchange capacity ranged from 19 cmol (p^+) kg^{-1} in Vertisol 3 (pH 9.3) to 37 cmol (p^+) kg^{-1} in Vertisol 2 (pH 8.2). An analysis of the data on N losses in relation to cation exchange capacity, however, did not show any clear pattern in this study. This indicates that cation exchange capacity does not provide efficient control of NH_3 losses from surface-applied urea, even at higher values. These results are consistent with those obtained by Fenn and Kissel (1973), which showed that NH_3 losses from Houston black clay reached 50% at a cation exchange capacity of 58 cmol (p^+) kg^{-1} soil. The soil cation exchange capacity is important because it provides a mechanism by which NH_4^+ is removed from the soil solution, thereby reducing NH_3 volatilization (Hargrove 1988). A substantial reduction in NH_3 losses due to a high cation exchange capacity may occur when N fertilizers are incorporated into soil. However, the results of the present study did not give any indication of such a mechanism in spite of the wide variation in cation exchange capacity in these soils.

Similarly, the effect of electrical conductivity on N losses was not clearly demonstrated in the present study. The electrical conductivity increased with pH (Table 1), the maximum value in Vertisol 3 (1.3 dS m^{-1}) being associated with the highest pH value (9.3). Among soil factors, pH is considered more important than electrical conductivity in regulating N losses through NH_3 volatilization. Hence, when pH is as high as 9.3, the electrical conductivity (e.g., 1.3 dS m^{-1}) may have not effect. However, in the present study, N losses from Vertisol 1, with an electrical conductivity as low as 0.1 dS m^{-1}, were almost equal to those from Vertisol 3, with an electrical conductivity as high as 1.3 dS m^{-1} (Table 3). Thus, electrical conductivity had no appreciable effect on NH_3 volatilization in these soils.

In conclusion, losses through NH_3 volatilization from Vertisols following urea applications onto the soil surface followed by moisture treatments equivalent to near field capacity or frequent light rainfalls. Therefore, fertilizer N management such as a split application and/or placement of urea materials (e.g., S-coated urea, reactive layer-coated urea, etc.), may help to reduce N losses and to make dry-seeding technology more effective in allowing higher yields. However, in pastures, orchards, and in zero-tilled surfaces, urea is generally applied on the surface. If a suitable technology can be devised to minimize NH_3 losses

with surface urea placement, a basic economic advantage will be obtained by increasing N efficiency and lessening adverse environmental impacts.

References

Al-Kanani T, MacKenzie AF, Fyles JW, Ghazala S, O'Halloran IP (1994) Ammonia volatilization from urea amended with lignosulfonate and phosphoroamide. Soil Sci Soc Am J 58:244–248

Avnimelech Y, Lahar M (1977) Ammonia volatilization from soils: Equilibrium considerations. Soil Sci Soc Am J 41:1080–1084

Bouwmeester RJB, Vlek PLG, Stumpe JM (1985) Effect of environmental factors on ammonia volatilization from a urea-fertilized soil. Soil Sci Soc Am J 49:376–381

Bremner JM (1965) Inorganic forms of nitrogen. In: Black CA, Evans DD, White JL, Ensminger LE, Clarke FE (eds) Methods of soil analysis, part 2, 2nd edn. Agron Monogr 9, Am Soc Agron, Madison, Wis, pp 1179–1232

Bremner JM, Mulvaney CS (1982) Total nitrogen. In: Page AI, Miller RH, Keeney DR (eds) Methods of soil analysis. Part 2, 2nd edn. Agron Monogr 9, Am Soc Agron, Madison, Wis, pp 595–624

Craig JR, Wollum WG II (1982) Ammonia volatilization and soil nitrogen changes after urea and ammonium nitrate fertilization of *Pinus taeda* L. Soil Sci Soc Am J 46:409–414

Day PR (1965) Particle fractionation and particle-size analysis. In: Black CA, Evans DD, White JL, Ensminger LE, Clarke FE (eds) Methods of soil analysis, Part 1. Agron 9, Am Soc Agron, Madison, Wis, pp 545–566

El-Swaify SA, Pathak P, Rego TJ, Singh S (1985) Soil management for optimized productivity under rainfed conditions in the semi-arid tropics. Adv Soil Sci 1:1–64

Ernst JW, Massey HF (1960) The effects of several factors on volatilization of ammonia formed from urea in the soil. Soil Sci Soc Am Proc 24:87–90

Fan MX, Mackenzie AF (1993) Urea and phosphate interactions in fertilizer microsites: Ammonia volatilization and pH changes. Soil Sci Soc Am J 57:839–845

Fenn LB, Hossner LR (1985) Ammonia volatilization from ammonium or ammonium-forming nitrogen fertilizers. Adv Soil Sci 1:123–169

Fenn LB, Kissel DE (1973) Ammonia volatilization from surface applications of ammonium compounds on calcareous soils. I. General theory. Soil Sci Soc Am Proc 37:855–859

Ferguson RB, Kissel DE (1986) Effects of soil drying on ammonia volatilization from surface applied urea. Soil Sci Soc Am J 50:485–490

Freney JR, Simpson, JR, Denmead OT (1983) Volatilization of ammonia. In: Freney JR, Simpson JR (eds) Gaseous loss of nitrogen from plant–soil systems. Martinus Nijhoff/Dr W Junk, The Hague, pp 1–32

Hargrove WL (1988) Evaluation of ammonia volatilization in the field. J Prod Agric 1:104–111

Hignett TP (1979) Fertilizer manual. Reference manual. IFDC-R-1 International Fertilizer Development Center. Muscle. Shoals, Ala

Jackson ML (1967) Soil chemical analysis. Prentice Hall of India Pvt Ltd, New Delhi, India

Jayakumar GWL (1992) Urea hydrolysis in semi-arid tropical Alfisols and Vertisols. PhD thesis, APAU Hyderabad, India

Kanwar JS, Kampen J, Virmani SM (1978) Soil and water conservation and utilization for increased food production in the semi-arid tropics. In: Proc 11th Congr Soil Sci, Edmonton, Canada, Trans. Int Soc Soil Sci, Wageningen, 1:95–118

Mahendrappa MK, Ogden ED (1973) Pattern of ammonia volatilization from a forest soil. Plant and Soil 38:257–265

McInnes KJ, Ferguson RB, Kissel DE, Kanemasu E (1986) Field measurements of ammonia loss from surface applications of urea solutions to bare soils. Agron J 78:192–196

Sahrawat KL (1984) Effects of temperature and moisture on urease activity in semi-arid tropical soil. Plant and Soil 78:401–408

Simpson JR (1968) Losses of urea nitrogen from the surface of pasture soils. In: Proc 9th Int Congr Soil Sci, Adelaide, Australia, Trans. Int Soc Soil Sci, Wageningen, 2:459–466

Terman GL (1979) Volatilization losses of nitrogen as ammonia from surface-applied fertilizers, organic amendments and crop residues. Adv Agron 41:189–223

Vlek PLG, Stumpe JM (1978) Effect of solution chemistry and environmental conditions of ammonia volatilization losses from aqueous systems. Soil Sci Soc Am J 42:416–421

Walkley A, Black IA (1934) Estimation of soil organic carbon by the chromic acid titration method. Soil Sci 47:29–38

Whitehead DC, Raistrick N (1990) Ammonia volatilization from five nitrogen compounds used as fertilizers following surface application to soils. J Soil Sci 41:387–394

Xu JG, Heeraman DA, Wang Y (1993) Fertilizer and temperature effects on urea hydrolysis in undisturbed soil. Biol Fertil Soils 16:63–65