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SUPPRESSION OF AMMONTA VOLATILIZATION FROM UREA THROUGH FERTILIZER MODIFICATIONS : I. EFFECT OF AMMONIUM SALTS

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The effect of amonium chloride, ammonium sulphate and ammonium nitrate on ammonia volatilization loss from urea applied in alluvial alkaline soil was studied under the laboratory conditions. These ammonium salts suppressed the ammonia loss. Ammonium nitrate was the most effective and it suppersed the ammonia loss by about 90% when mixed with urea in the ratio of 2 : 1 (urea : ammonium nitrate, on N equivalent basis). The effect of different proportions of urea and ammonium nitrate on ammonia loss was also studied. A highly significant positive correlation coefficient ($r = 0.976$) was found between the ratios of urea : ammonium nitrate and the loss of ammonia. The following euuation describes the regression line :

$$Y = 2.561\ x - 0.655$$

Slowing down of urea decomposition and stimulation of nitrification by ammonium salts resulted in suppression of ammonia loss from urea.

INTRODUCTION

At present, over 80 per cent of the N fertilizer in Pakistan is urea. A disadvantage of urea is the risk of volatilization of ammonia from soil surface, following urease mediated hydrolysis of urea to ammonium. Volatiliz ation losses may be especially large from soils with high pH and with low cation exchange capacity particularly if the soil is warm and drying when urea is applied (Gasser, 1964 ; Ernst and Massey, 1960). Since all these conditions prevail in Pakistan soils 30 per cent of urea nitrogen is lost as ammonia (Hamid and Ahmad, 1987). Higher fertilizer and energy costs and the need to maintain the quality of global

environment provide powerful incentives for using agricultural N more efficiently. In this endevour the control of ammonia loss is of prime importance. Thus the development of an effective chemical that can retard urea hydrolysis in soil is a major N research goal of soil scientists.

Numerous chemicals have been tested for their potential as urease inhibitors for use with animal feed containing urea or with urea fertilizer. Among the compounds proposed for use with urea fertilizer are piridine-3-Sulphonic acid, O.chloro-p amino benzoic acid, andr-benzene hexachloride (Peterson and Walter, 1970) dithiocarbamate (Hyson, 1963; Tomlison 1967), urea derivatives such as methyl urea, dimethyl urea, thiourea or phenyl urea (Sor *et al.* 1966; Geissler *et al.* 1970) mercaptans (Gould *et al.* 1978) quinones and polyhydric phenols (Anderson, 1969;1970) and hydroquinone (Rodger and Pruden, 1984). Of more than 100 compounds tested as soil urease inhibitors Bremner and Douglas (1971) found that dihydric phenols and quinones were the most effective organic compounds and that silver and mercury salts were the most effective inorganic compounds. The cost of production of these compoundsl imits their use in the field with fertilizer. Hence there is a need of developing simple economical means and methods of controlling the ammonia loss from urea fertilizer. The objective of our research, therefore, was to test the effectiveness of ammonium salts on ammonia loss reduction compared with application of urea alone.

MATERIALS AND METHODS

The laboratory experiments were conducted on alluvial alkaline calcareous sandy loam soil (obtained from surface 30 cm layer) which was 10.2% clay, 11.0% silt and 78.8% sand with pH 8.0, O. M. 0.83% and $CaCO_3$ 3.53%.

The experimental apparatus for collecting ammonia volatilized from the fertilized soil consisted of an acid trap, water trap (humidifier), soil chamber (Erlenmeyer Flask) ammonia collection vessel containing 50 ml of 4% H_3BO_3 solution with bromcresol green and methyl red indicators. An air comressor was used in moving the air across the sample surface.

As soon as the nitrogen was added to the soil, compressed air scrubbed through 0.5 N H_2SO_4 and then through water was passed into the flasks. This air had sufficient humidity to keep the moiture in soil at a constant level. Air

left the flasks (1.5 l/h) through the glass tubing and passed into the boric acid solution. Capillary tubes were used at this point to equalize the pressure in the system. The ammonia was absorbed in the boric acid solution which was back titrated against standard H_2SO_4.

Air dried samples of soil (500 g) were placed in 1 l Erlenmeyer Flasks. The surface area of soil was 113.1 cm^2 in the flasks. The soil was moistened with enough water to bring the water content of soil to 1/3 W. H C. Nitrogen was applied to the surface of soil. The amount of N applied was equivalent to 120 kg/ha (on area basis). The measurements were made at room temperature (26 $\pm$ 3°C).

Initially mixtures of urea and ammonium salts were prepared by mixing 2 parts of urea and 1 part of ammonium salts (on N equivalent basis) Urea and mixtures of urea with ammonium salts were applied to soil in solution. Then mixtures of urea and ammonium nitrate were prepared to obtain the ratios of 9 : 1, 4 : 1, 3 : 1, 2 : 1 and 1 : 1 (urea : ammonium nitrate on N equivalent basis). Ammonia losses were measured from these mixtures and urea.

Mineral N in soil at different intervals of incubation was also determined. For estimation of mineral N soil was extracted with 2 M KCl by shaking for 30 minutes. Extracts were then filtered and analyzed for NH_4- and NO_3-N by steam distillation (Bremner and Keeney, 1966).

RESULTS

The cumulative volatilization losses from soil fertilized with urea and mixtures of urea and ammonium salts (NH_4Cl, $(NH_4)_2SO_4$ and NH_4NO_3) are shown in Fig. 1. During 38 days of the experiment 28% of the applied nitrogen was volatilized from urea alone. Mixing ammonium salts with urea significantly reduced the ammonia losses. Ammonium chloride reduced the ammonia loss by 44%, ammonium sulphate reduced the loss by 30% and ammonium nitrate reduced the loss by 90%.

The volatilization losses from mixtures of urea and ammonium nitrate having urea : ammonium nitrate ratios of 9 : 1, 4 : 1, 3 : 1, 2 : 1 and 1 : 1 are given in Fig. 2. It is evident from the curves that increasing the proportion of

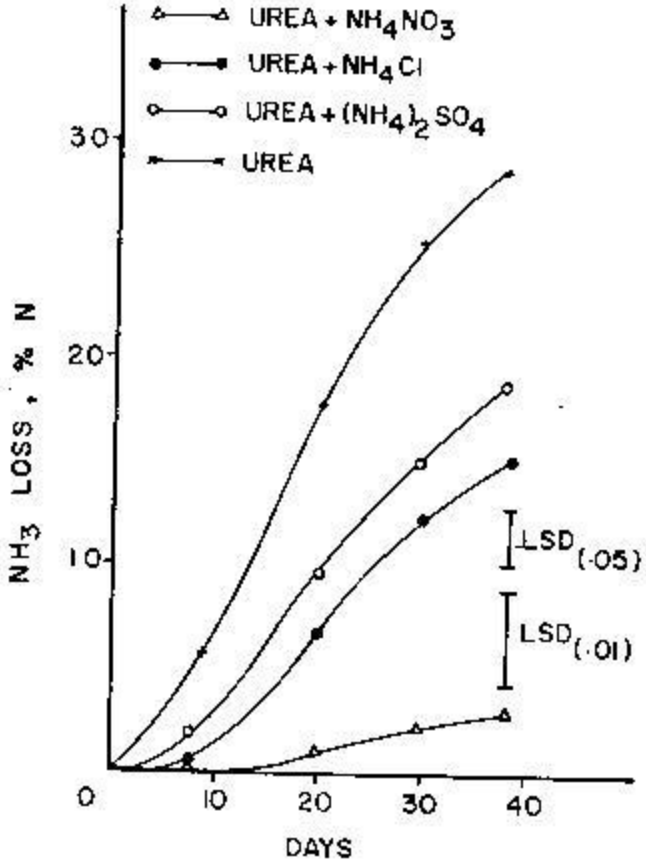

Fig. 1 · Effect of ammonium salts on ammonia volatilization from urea in soil

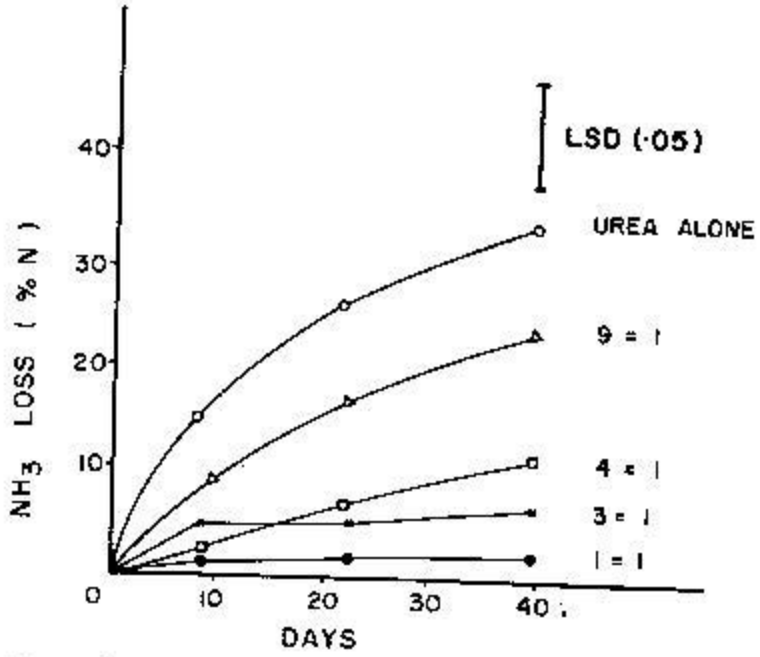

Fig. 2 · Effect of Mixing NH_4NO_3 with Urea on NH_3 Loss

ammonium nitrate in the mixture resulted in increased reduction in volatilization loss. At 1 : 1 ratio of urea : ammonium nitrate only 2% loss of ammonia was observed which corresponded to 95% reduction in ammonia loss. Over a period of 40 days loss of ammonia from 3 : 1 mixture of urea : ammonium nitrate was 6% and that from urea was 31.2%. The widest ratio of urea to ammonium nitrate that could reduce ammonia loss by 25% was 9 : 1. A highly significant positive correlation coefficient (r = 0.976) was found between the ratios of urea to ammonium nitrate and the loss of ammonia (Fig. 3). The following equation describes the regression line :

$$Y = 3.561\ x - 0.655$$

The estimation of mineral N at different intervals of incubation showed that NH_3- and NH_4-N was consistently higher in urea alone treatment as compared to mixture of urea and ammonium nitrate: but the differences were statistically non-significant (Table 1). Hower, NO_3-N was significantly higher in case of mixture of urea and ammonium nitrate as compared to urea alone (Table 1, P = 0.05).

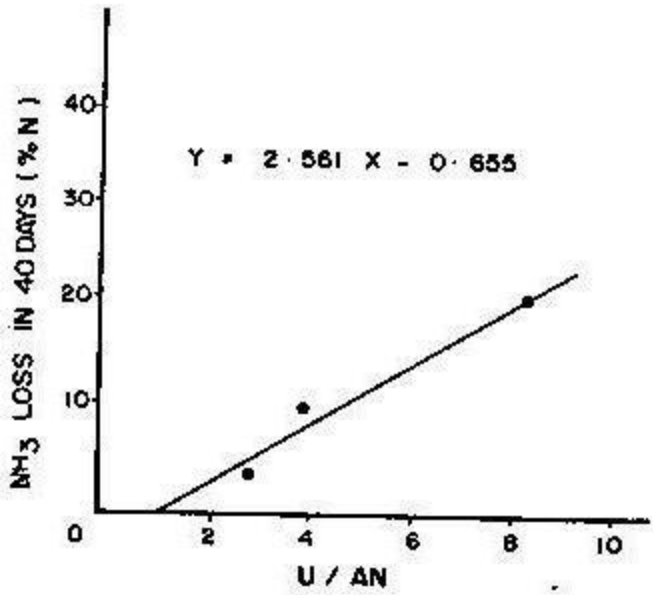

Fig. 3 - Relationship Between NH_3 Loss and Ratio of Urea to Ammonium Nitrate (U/AN)

Table 1 : *Effect of ammonium nitrate on mineralization of urea in alluvial alkoline soil.*

Time days		Mineral nitrogen, mg N 1000g^{-1} soil					
		NH_3		NH_4		NO_3	
		Urea	U+AN	Urea	U+AN	Urea	U+AN
d_1		1.31	1.11	22.30	20.83	4.32	10.49
	't'	0.971 NS		1.73 NS		6.329*	
d_2		5.90	3.93	57.07	53.13	9.84	15.08
	't'	2.696 NS		3.43 NS		4 393*	
d_7		13.12	8.52	72.81	68.22	12 46	16.40
	't'	1.99 NS		1.0341 NS		4.407*	
d_9		14 67	12 64	82.00	74.18	12.46	19.02
	't'	1.620 NS		2.497 NS		4.788*	
d_{22}		21.82	18 35	90.52	80.52	12.21	20.33
	't'	1.047 NS		2.932 NS		8 40*	

U+AN = Urea + ammonium nitrate NS = Non-significant.

* Significant at P = 0.05.

DISCUSSION

Urea when applied soil to first reacts with urease to from ammonium carbonate as follows :

$$CO(NH_2)_2 + 3H_2O \xrightarrow{\text{urease}} (NH_4)_2CO_3.H_2O$$

Ammonium carbonate is an unstable compound and decomposes according to the following reactions :

$$(NH_4)_2CO_3\,H_2O \longrightarrow 2NH_4OH + CO_2\uparrow$$

$$NH_4 + OH \leftrightharpoons NH_4OH \leftrightharpoons NH_3\uparrow + H_2O$$

Ammonium carbonate creates microsites in the vicinity of urea particle having high ammonium concentration and pH. It is with in these microsites that volatilization of ammonia occurs (Gasser, 1964).

The addition of Ca, Mg, K salts with urea has been found to substantial by reduce ammonia losses (Fenn *et al.*, 1981, 1987; Rappaport and Axley, 1984; Rheinbaben 1987) due to (1) the reductive effect on the urea microsite pH, (2) the reaction of $(NH_4)_2CO_3$ with Ca forming $CaCO_3$ and (3) a substential decrease in the urea hydrolysis rate (Fenn *et al.* 1981).

Similarly Kresge and Satchell (1960) and Watkins *et al.* (1972) observed reduction in ammonia losses from urea by mixing ammonium nitrate and ammonium chloride with urea. But they did not give any diffinitive explanation in regard to possible effects of these salts on ammonia losses.

In our study the ammonium salts also proved effective in reducing the ammonia losses. We observed an extensive lag phase in hydrolysis of urea when mixed with ammonium salts. The extensive lag phase resulted due to delayed decomposition of urea which had a regulatory effect on pH of soil-urea microsite and this was the condition that retarded the ammonia loss. In addition to this the stimulatory effect of NH_4 ion of ammonium salt on nitrification, prior to hydrolysis of urea, might also play a role in reducing the accumulation of excess ammonia and thus suppress the ammonia volatization.

On the basis of results of our study we conclude that ammonium salts especially ammonium nitrate is an effective inhibitor of ammonia volatilization from urea and its use is made more attractive by the fact that the inhibitor has a value as a fertilizer material. Like other salts (Terman and Fleming, 1968) ammonium nitrate could be used to produce an addition compound or an adduct with urea for overcoming the risk of ammonia volatilization losses from urea and getting the higher efficiency of fertilizer in alluvial alkaline soils.

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