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Volatilization of ammonia from urea-ammonium nitrate solutions as influenced by organic and inorganic additives

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Abstract

Fertilizers containing urea can suffer from nitrogen (N) loss through ammonia volatilization, resulting in reduced effectiveness of the fertilizers. The loss of N may be reduced by use of organic or inorganic additives.

Laboratory experiments were conducted on surface soil samples (0–15 cm) from two agricultural soils (St. Bernard and Ste. Sophie) to determine the impact of ammonium thiosulfate (ATS), boric acid, and a humic substance from leonardite, on NH_3 losses from surface-applied urea-ammonium nitrate (UAN) solutions. Experiments were carried out using moist soil samples in closed containers. Evolved NH_3 was carried out of the containers and trapped in boric acid solution using an ammonia-free humidified air flow.

Total NH_3 losses in these experiments ranged from 12.1 to 21.3% of the N applied. The reduction in NH_3 volatilization (expressed as % of added N) due to additives ranged from 13.6 to 38.5% and 3 to 36.3% in St. Bernard and Ste. Sophie soils, respectively. More NH_3 volatilized from the boric acid or humic treated UAN solutions than from ATS-UAN solutions.

Boric acid, ATS, and the humic substance, all significantly reduced urea hydrolysis in both soils in comparison to the untreated UAN solution. Further, the humic substance and boric acid treatment induced significant reduction in NO_3-formation. The results suggest that humic substance and to a lesser extent boric acid may function as urease and/or nitrification inhibitors. ATS treatment, particularly at higher levels increased NO_3-formation in both soils. The reason for this increase in nitrate formation is not clear.

Nitrogen (N) fertilizer solutions containing urea (U) can suffer from N loss through ammonia (NH_3) volatilization (Fenn and Hossner, 1985; Gascho, 1986; AL-Kanani et al., 1989). The efficiency of N fertilizer may be improved substantially if NH_3 losses are reduced. This may be achieved through the manipulation of the urea-ammonium nitrate (UAN) ratios and/or additives in the N solution (AL-Kanani et al., 1989). The volatilization of NH_3 can be reduced by increasing ammonium nitrate (AN) proportions in UAN solution (AL-Kanani et al., 1989). However, this reduces total N content of the UAN solution due to salting out effects. Chemical additives to UAN solution may help reduce potential loss of NH_3. Several organic and inorganic additives have been used to reduce NH_3 volatilization from N solutions. Soil enzyme inhibitors (Bremner and Douglas, 1971; Broadbent et al., 1985; Goos, 1985; Tomar et al., 1985; AL-Kanani et al., 1989), soluble calcium and potassium salts (Fenn et al., 1981; Fenn et al., 1982; Rappaport and Axley, 1984; Gascho, 1986), and urea phosphate [$CO(NH_2)_2.H_3PO_4$] (Bremner and Douglas, 1971; Stumpe et al., 1984; Fenn and Richards, 1986; Keller and Mengel, 1986; Urban et al., 1987; Bundy and Oberle, 1988) were the most common additives used. It should be noted, however, that the additive should not decrease total N content in the final UAN solution.

Although recent attention has been given to the ammonium thiosulfate (ATS) solution (Goos, 1985; Gascho, 1986; Janzen and Bettany, 1986; Sullivan and Havlin, 1988; AL-Kanani et al., 1989), another additive-humic substance (commercially known as Energizer[1], Mammoth Int. Chemical Co., Huston, Texas) or boric acid may be helpful in making N solution applications more efficient by slowing or preventing N loss from surface-applied UAN solution. Moreover, it is preferable that the additive used should also provide more nutrients. Schnitzer (1985) stated that 'humic substances act as suppliers and storehouses of nitrogen for plant roots and microorganisms'. Beside its N content, Energizer may contain other fertilizer nutrients due to its ability to form water-soluble metal and ligand complexes. Karcher (1963) cited by Aitken et al. (1964) indicated that the humic substance from leonardite contained the following nutrients: 1.55 calcium, 0.35 sodium, 0.13 iron, 0.095 magnesium, 0.016 copper, 0.006 manganese, 0.006 zinc, 0.0015 boron, and 0.0008% molybdenum.

The objective of this study was to evaluate the effectiveness of added ammonium thiosulfate, added humic substance (Energizer), and added boric acid on NH_3 losses from UAN solution surface-applied to soil.

Materials and methods

Surface soil samples (0–15 cm) from two eastern Canadian soils were obtained from cultivated corn fields. The soils used were St. Bernard (Typic Hapludoll) and Ste. Sophie (Typic Cryochrept) from Quebec (Table 1). Soils were air-dried, ground to pass a 2-mm sieve. The pH was determined in distilled water (1:1) using a single probe electrode. Analysis of particle size was carried out according to the hydrometer method (McKeague, 1976). Organic matter was determined by the Walkley-Black procedure (Nelson and Sommers, 1982), total soil N was determined by the Kjeldahl method (Bremner and Mulvaney, 1982), and phosphorus and potassium were extracted using the Mehlich III procedure (Mehlich, 1984).

Table 1. Some physical and chemical properties of soil samples

	Soil	
	St. Bernard	Ste. Sophie
Clay ($g\ kg^{-1}$)	219 (scl)	87 (s)
Organic matter ($g\ kg^{-1}$)	38.3	25.3
Total N ($g\ kg^{-1}$)	2.7	1.3
pH	6.5	5.9
Extractable K ($mg\ kg^{-1}$)	40.0	108.0
Extractable P ($mg\ kg^{-1}$)	9.0	32.0

UAN solution containing 10% total N by weight derived from U and AN was used. The proportion, as percentage, of total N was 50% urea (U) and 50% ammonium nitrate (AN). Two levels, 1.8 and 3.6% (by weight of UAN solution), of boric acid and commercial 60% ATS or 1.7 and 3.4% of the 0.1% (w/v) Energizer were used. Prior to N solution application, deionized distilled water was applied uniformly with a pipette to moisten air-dry samples (44 to 47 g), and to produce water potential equivalent, at equilibrium, of −0.01 MPa. Soil water was not replenished during the incubation period. Ten minutes after addition of water to soil, dropwise surface application of 400 μL of N solutons was initiated. N solutions increased the soil moisture by 1%. The rate of N applied was equivalent to 147 $kg\ ha^{-1}$, calculated on a surface area basis. Methods of ammonia loss determination and soil inorganic N recovery are described elsewhere (AL-Kanani et al., 1989).

The Energizer (kindly supplied by Dr. Simon A. Visser, Department of Soils, Laval University, Quebec) originated from Leonardite. The functional group analysis of the Energizer was as follows: 67.7 C, 23.0 O, 5 H, 1.7 N, 0.4 S and

[1] Trade name used in the text is included for the reader's convenience and do not constitute any preferential endorsement of the product named over similar products available on the market.

<2.2% ash; 14.2 CO_2H, 2.3 alcoholic OH, 2.1 phenolic OH, 1.8 ketonic C = O, 0.3 quinonoid C = O, and 0.2 OCH_3 mol kg^{-1} (Ogner and Schnitzer, 1971). The pH of the 0.1% Energizer solution (w/v) was 7.7.

Results and discussion

Addition of humic substance (Energizer), ATS, and boric acid to a 50–50 UAN solution reduced NH_3 losses (Table 2). The reduction in NH_3 volatilization, when compared with the untreated solution (UAN), ranged from 13.6 to 38.5 and 3 to 36.3% for the 1.8% boric acid and 1.8% + 1.7% Energizer treatments in St. Bernard and Ste. Sophie soils, respectively (Table 2). The magnitude of NH_3 volatilized from the boric acid or Energizer treated UAN solution was slightly more than that observed in ATS-UAN solutions. Energizer and to a lesser extent boric acid may function as urease and/or nitrification inhibitors. Both ATS and boric acid have been found to reduce NH_3 volatilization due to their inhibitory effect on the urease enzyme (Nommik, 1973; Goos, 1985). However, very little is known about the influence of humic substances on NH_3 volatilization and nitrification.

Energizer, when added to UAN, resulted in significant reduction in the volatilization of NH_3 in comparison to untreated UAN solution (Table 2). This is probably due to an inhibitory effect of humic substance on the enzyme urease. It has been suggested that soil urease can be trapped within humic substances (Pettit et al., 1976). Several mechanisms have been suggested to describe humic-enzyme interactions (Butler and Ladd, 1969; Bremner and Douglas, 1971; Burns et al., 1972; Ceccanti et al., 1978; Pflug and Ziechmann, 1981; Tomar and MacKenzie, 1984). These mechanisms include: 1) binding of the enzyme by functional groups (i.e. carboxyl, phenolic hydroxyl and quinones) from the humic substance, 2) interaction of the humic substance with the substrate, which reduces the affinity of the enzyme for its substrate, and 3) a distortion in the structure of the enzyme molecule due to inherent rigidity of the high molecular weight humic substances, which reduce the activity of the enzyme. Because of the intimate relationship between the urease activity, urea hydrolysis, and NH_3 volatilization, it is likely that these mechanisms would have pronounced effects on the loss of N from UAN solution surface-applied to soil. Bremner and Douglas (1971) and Tomar and MacKenzie (1984) found that p-benzoquinone, which may exist in humic substances in variable proportions, induced significant reduction in urea hydrolysis.

When combined with ATS, both boric acid and Energizer caused further reduction in NH_3 volatilization (Fig. 1). However, there was no further benefit from higher levels of ATS and Energizer (Fig. 1). This was probably due to the increase of N solution pH caused by the addition of high rates of ATS and Energizer (data not shown).

Table 2. Effect of ammonium thiosulfate (ATS), Energizer, and boric acid on ammonia volatilization from UAN solution

N solution	Soil	
	St. Bernard	Ste. Sophie
	—— NH_3–N volatilized as % of total N[1] ——	
UAN	21.3[2] a	19.0 a
UAN + 1.7% Energizer	16.8 bc	16.1 b
UAN + 3.4% Energizer	17.0 c	15.7 b
UAN + 1.8% boric acid	18.4 b	18.4 a
UAN + 3.6% boric acid	16.8 c	16.0 b
UAN + 1.8% ATS	14.5 d	12.6 d
UAN + 3.6% ATS	13.4 e	14.3 c
UAN + 1.8% ATS + 1.7% Energizer	13.1 e	12.1 d
UAN + 1.8% ATS + 1.8% boric acid	13.7 de	13.1 cd

[1] ammonia volatilized after 10 days of incubation.
a–e Means within a column of each soil followed by the same letter are not significantly different at p = 0.05 by Duncan's new multiple range test.
[2] to calculate values as percentage of NH_3 loss per added urea multiply by 2.

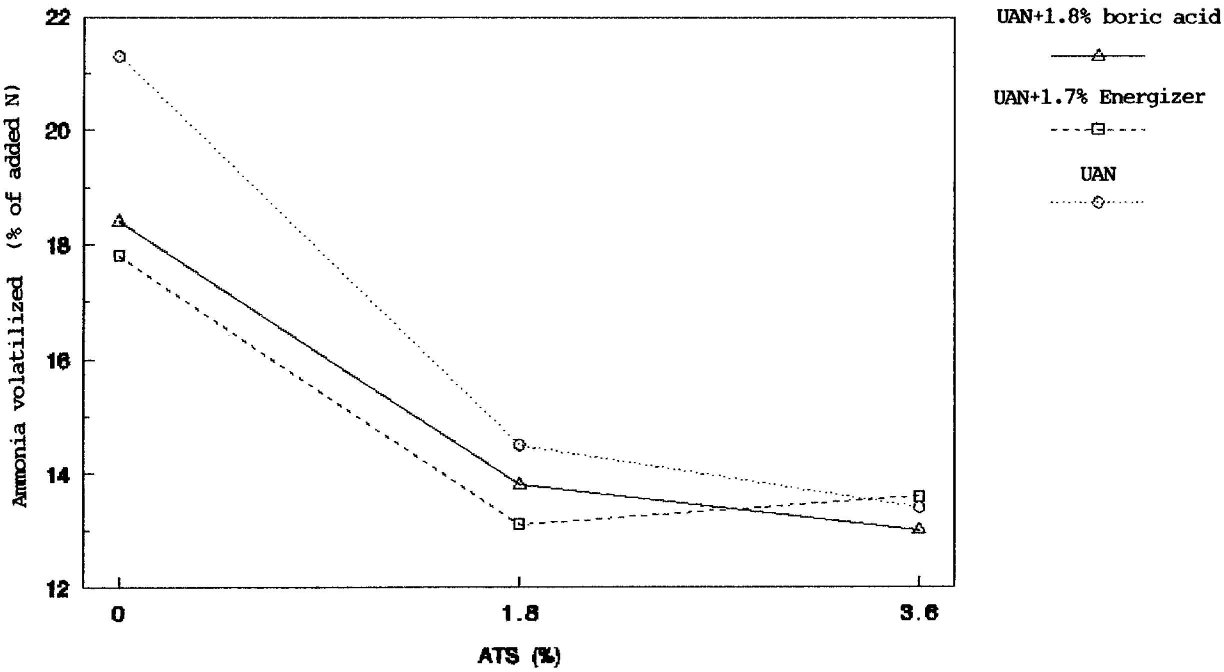

Fig. 1. Effects of ATS, boric acid, and Energizer on ammonia losses from UAN solutions surface-applied to St. Bernard soil.

Acidification of 1.8% ATS-UAN and 1.7% Energizer-UAN solutions with nitric acid was not successful. Nitric acid caused a murky solution with ATS-UAN or sedimentation of coagulated colloids with the Energizer-UAN solution. However, acidification of untreated UAN and boric acid-UAN solutions with nitric acid did reduce NH_3 volatilization in both soils (Fig. 2).

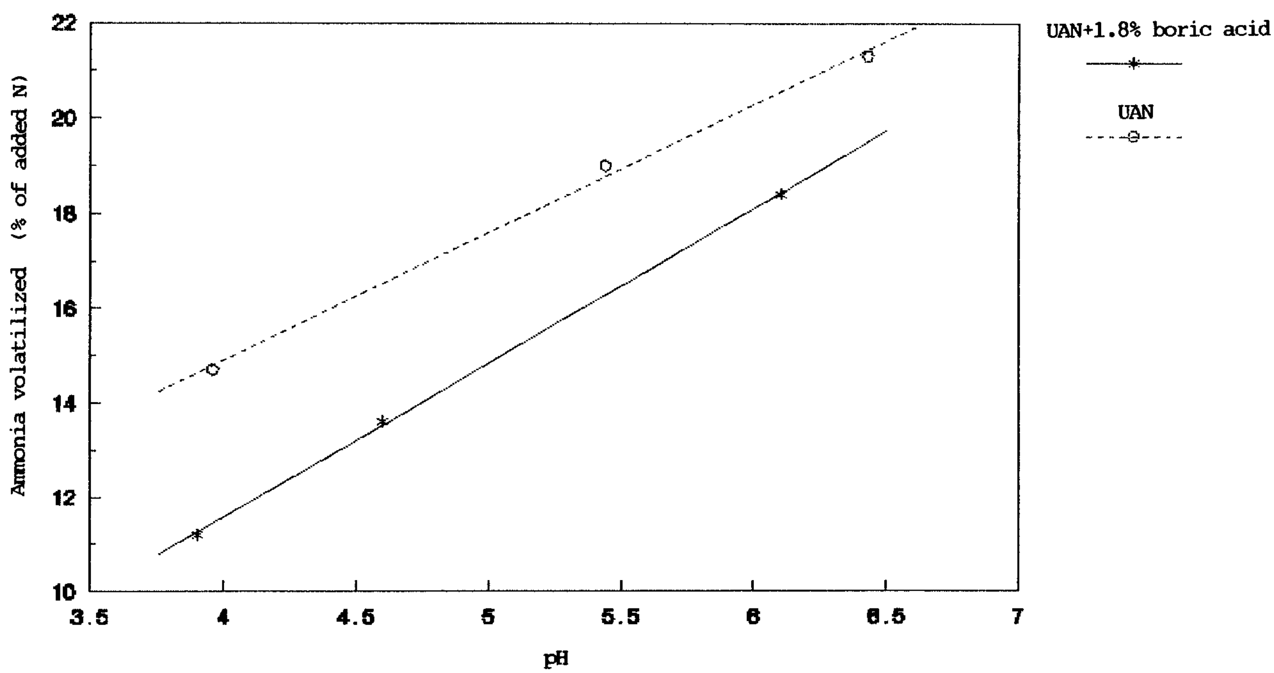

Fig. 2. The effect of UAN solution pH on ammonia loss from St. Bernard soil (regression lines, for UAN-boric acid, $Y = -1.47 + 3.261x$; $R^2 = 0.999$; for UAN, $Y = 4.14 + 2.69x$; R^2 0.997).

A significant linear relationship between NH_3 volatilization and the pH of the UAN or boric acid-UAN solution was observed in both soils (Fig. 2). The pH of the soil suspension after incubation was not related to NH_3 volatilization in both soils (data not shown), indicating that any solution pH effect was either localized or of short term.

Several investigators found that ATS inhibits both urea hydrolysis and nitrification (Goos, 1985; Janzen and Bettany, 1986). However, toxicity was the major drawback to the use of ATS as a fertilizer and/or nitrification inhibitor particularly at higher rates of ATS (Goos, 1985; Janzen and Bettany, 1986). This toxicity was probably due to NO_2^- accumulation (Janzen and Bettany, 1986). Although the question of Energizer toxicity was not addressed in this paper, our research effort will continue to study the effect of humic substances including Energizer on the plant growth and the results will be reported in a follow-up paper. It is worth mentioning here, however, that some humic substances have been found to exert a stimulating effect on radish seed (*Raphanus sativus*) germination, the oat mesocotyl, elongation of both the root and shoot of green pepper (*Capsicum annuum*), and lettuce hypocotyl elongation (Petrovic et al., 1982).

Boric acid, ATS, and Energizer, all significantly reduced urea hydrolysis in both soils in comparison to the untreated UAN solution (Table 3). This is in agreement with the findings of Nommik (1973), Malhi and Nyborg (1979), and Goos (1985) who suggested that boric acid and ATS function as general metabolic inhibitors

Table 3. Effects of humic substance (Energizer), boric acid, and ammonium thiosulfate (ATS) on forms of inorganic N recovered in the soil from UAN solutions

Soil and N solution	N extracted from soil after 10 day				Inhibition of	
	Urea–N	NH_4–N	NO_3–N	NO_2–N	Urea hydrolysis[1]	NO_3[3]
	— % N of added N —				— % —	
St. Bernard						
UAN	0.18	42.4	20.0	ND	0	0
UAN + 1.7% Energizer	8.40	41.1	14.2	0.4	16	29.0
UAN + 3.4% Energizer	11.0	40.4	14.9	0.3	22	25.5
UAN + 1.8% boric acid	7.4	45.9	16.0	0.6	15	20.0
UAN + 3.6% boric acid	14.8	42.9	15.3	0.6	30	23.5
UAN + 1.8% ATS	11.1	58.6	20.5	0.7	22	(2.6)
UAN + 3.6% ATS	12.3	58.2	22.4	0.8	25	(12.0)
UAN + 1.8% ATS + 1.7% Energizer	13.1	49.1	15.7	0.4	26	21.5
UAN + 1.8% ATS + 1.8% boric acid	13.8	47.2	17.1	0.8	28	14.5
LSD[2]	2.1	5.2	3.1	0.4	3	4.1
Ste. Sophie						
UAN	0.1	46.2	19.3	0.3	0	0
UAN + 1.7% Energizer	2.5	39.7	12.7	0.2	5	34.2
UAN + 3.4% Energizer	5.7	40.1	12.7	0.2	11	34.2
UAN + 1.8% boric acid	2.4	46.0	16.3	0.3	5	15.5
UAN + 3.6% boric acid	6.1	45.3	15.7	0.2	12	18.7
UAN + 1.8% ATS	3.6	55.1	17.5	0.4	7	9.3
UAN + 3.6% ATS	4.3	53.5	20.2	0.5	9	(4.7)
UAN + 1.8% ATS + 1.7% Energizer	2.1	44.1	15.7	0.4	4	18.7
UAN + 1.8% ATS + 1.8% boric acid	3.1	49.3	16.9	0.5	6	12.4
LSD	1.1	4.7	1.9	0.1	4.4	2.3

[1] Percent urea hydrolysis inhibition was calculated as: percentage of urea-N recovered/50, where the 50 represents the percentage of urea-N in the 50–50 UAN solution used.
[2] Least significant difference at $p = 0.05$.
[3] Reduction in the formation of NO_3, when compared to untreated UAN solution. Figure in parenthesis refers to the percentage increase in nitrification.

rather than specific urease inhibitors. Similarly, Energizer may function as a general metabolic inhibitor. There was no relationship between NH_4^+ disappearance and NO_3^- formation regardless of additive treatments (Table 3). The lack of a relationship between ammonium disappearance and nitrate formation may be attributed to an ammonium fixation, volatilization, or incorporation in soil organic matter.

Boric acid treatment induced significant reduction in NO_3^- formation (Table 3). This is in agreement with the finding of Nommik (1973). The results also showed a significant inhibitory effect of Energizer on nitrification. Although the reason for this nitrification inhibition is not clear, one might consider the following hypotheses 1) free radicals of humic substance are known to be important participants in biological electron transfer processes (Atherton et al., 1967), allowing electron transfers to take place between various metabolic intermediates, thus influencing ammonium or nitrite oxidizing microorganisms (Janzen and Bettany, 1986) to variable degrees, and 2) ion sequestering by humic materials could delay the oxidation processes of ammonium or nitrite. Surprisingly, the ATS treatment, particularly at higher levels increased NO_3^- formation in both soils (Table 3). Although the reason for this increase in nitrate formation is not clear, it may be attributed to the increase in ammonium concentration at higher levels of ATS. However, for some ATS treatments applied to Weyburn loam soil, Janzen and Bettany (1986) have also found relative increases in nitrate formation with added ATS.

Conclusions

The addition of the humic substance, Energizer, to UAN solution significantly reduced NH_3 loss. This was probably due to the inhibitory effect of Energizer on urea hydrolysis. Further, the results indicated that the Energizer may also behave as a nitrification inhibitor. Beside these functions of the Energizer, its low cost and possibly less toxic effect on the environment render the Energizer more practical to be used in fertilizer industries in comparison to other metabolic inhibitors like boric acid and ATS currently available in the market. However, the mechanism in which Energizer inhibits urea hydrolysis of nitrification in the soils studied is not known, and thus needs to be evaluated. One also needs to study humic substances from different sources (i.e. composts, microbial cultures, aquatic environment, etc.) in order to provide more information about the effectiveness of humics as urease and nitrification inhibitors. Such information would allow better estimation of N fertilizer applications since humic compounds comprise appreciable fractions of organic matter in soils. Boric acid was also effective in reducing NH_3 volatilzation and nitrate formation. However, since the range between boron (B) deficiency and toxicity in soils is relatively narrow and because, at any one time, there is more B sorbed by soil than present in solution, one might exert extra precautions in using boric acid as a nitrification inhibitor. Although ATS was effective in reducing urea hydrolysis, possibly by acting as a urease inhibitor, its effectiveness as a nitrification inhibitor was very limited. Thus, the use of ATS as nitrification inhibitor in liquid fertilizer surface-applied to St. Bernard and Ste. Sophie soils needs further investigation.

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