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Effect of humic acid on ammonia volatilization from some calcareous soils

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Abstract. The objectives of this study were to compare the effect of three rates of humic acid (0, 2.5 and 5.0 g kg^{-1} soil) and N-urea (0, 60 and 120 mg N kg^{-1} soil) and mixtures of them on NH_3, loss (volatilization) from two calcareous soils (Abul-Khasseb, silty clay soil, and Zubair, loamy sand soil). The use of humic acid significantly reduced NH_3 loss and increased exchangeable NH_4^+ in both studied soils. The high total acidity of humic acid made the treatment the best in reducing N loss after incubation. Zubair soil showed more N loss than Abul-Khasseb soil due to their physical and chemical characteristics. The soil content of NH_4^+ and NO_3^- increased significantly in both studied soils with increasing N rates. It can conclude that, humic acid, in general have great ability in controlling NH_3 loss and retaining NH_4^+ in calcareous soils. It could be an economical efficient, practical and easiest way to control N loss.

Key Words: N-urea, N loss, urea fertilizer, ammonium, nitrate.

Introduction. Ammonia volatilization is a major pathway for N loss from surface-applied urea (Cai et al 2002; Prasertsak et al 2001). Volatilization losses can occur in calcareous soils due to high pH and NH_4^+ in the microsite where urea granules are dissolved and hydrolyzed (Siva et al 1999; Fan & Mackenzie 1993). Under normal conditions ammonium (NH_4^+), hydroxyl (OH^-) and carbonate ($CO_3^=$) ions are produced rapidly (1 or 2 days) after surface application of urea by urease (Zhengping et al 1991). This leads to the accumulation of NH_4^+ which simultaneously increases the soil pH surrounding the application area or near the urea granule (Zaman et al 2007). The increase of OH^-, HCO_3^- and NH_4^+ concentrations through this process plays a significant role in the rapid loss of nitrogen.

There are many factors involved in NH_3 volatilization, which can be grouped into soil (e.g. pH, CEC), environment (e.g. temperature, humidity) and management (e.g. surface application of fertilizer, drilling). A number of studied with different approaches has reduced NH_3 losses (Fan & Mackenzie 1993; Al-Kanani et al 1990; Purakayastha & Katyal 1998; Zaman et al 2007). Acidic materials alone, organic and inorganic additives, mixture of acidic materials and additives could reduce N losses by 60, 38.5 and 49 % respectively (Lethbride & Burns 1976; Al-Kanani et al 1990; Fan & MacKenzie 1993; Zaman et al 2007).

In some studies, acidic materials such as humic acid and triple super phosphate have been used to reduce ammonia loss from surface applied urea (Fan & Mackenzie 1993; Ahmed et al 2006). These acidic materials lower the soil microsite pH immediately around the fertilizer, reduce the hydrolysis of urea thus reducing the ammonia loss. Humic acid has high total acidity (CEC) aid to retain NH_4^+ and NO_3^- which are the plant useable from of nitrogen (Fan & Mackenzie 1993; Ahmed et al 2006). The objective of this study was to evaluate the effectiveness of humic acid in reducing N loss from urea fertilizer added to two calcareous soils as well as to investigate the ability of humic acid to retain NH_4^+, or reduce soil pH.

Material and Method. The study was conducted on two calcareous soils from Basrah governorate (Abul-Khasseb and Zubair-Barjesia). The soil samples taken at 0 – 30 cm depth were air dried and ground to pass 2 mm sieve. The selected chemical and physical properties of the soil were determined according to the methods mentioned iby Black (1965) and Sparks et al (1996) (Table 1).

Table 1

Some chemical and physical characteristics of soils and humic acid

Property	*Abul-Khasseb soil*	*Zubair soil*	*Humic acid*
pH (water)	7.7	8.0	-
EC (dS m $^{-1}$)	12.8	3.3	-
Total organic carbon (%)	8.220	3.02	55.10
Total nitrogen (%)	-	0.12	-
CEC (C mol kg $^{-1}$)	28.15	5.11	750
Sand (g kg $^{-1}$)	495.4	920.0	nd
Silt (g kg $^{-1}$)	59.3	18.9	nd
Clay (g kg $^{-1}$)	443.2	59.4	nd
Texture	Silty clay	Loamy sand	nd
Carboxylic group (Cmol kg $^{-1}$)	nd	nd	450
Phenolic group (Cmol kg $^{-1}$)	nd	nd	300
Total acidity (Cmol kg $^{-1}$)	nd	nd	750
Total carbonate (g kg $^{-1}$)	381.2	145.0	nd

nd – no data.

In order to investigate the effectiveness of humic acid in reducing N loss from urea fertilizer 100 g of air dried soil, grounded and sieved to pass through 2 mm size was placed into plastic containers (15 cm × 10 cm × 10 cm depth). The amounts of humic acid were used with three rates (0, 2.5 and 5.0 g kg^{-1} soil), and urea was applied to the soil surface with three rate (0, 60 and 120 mg N kg^{-1} soil) as urea (46 % N). Soils were moistened to field capacity (30 % for Abul-Khasseb soil and 18 % for Zubair soil). Released NH_3 captured in the trapping solution containing 25 mL boric acid bromocresol green and methyl red indicator. The incubation chamber was heated to 35°C. Boric acid indicator trans were replaced after (2, 10, 20, 30, 40 and 60 days), and buck titrated with 0.01 N HCl to estimate the NH_3 released. After each period incubation, soil samples were evaluated for pH, exchangeable NH_4^+ and available NO_3^- (Sparks et al 1996).

Results and Discussion. The chemical and physical characteristics of soils (Abul-Khasseb, silty clay, and Zubair, loamy sand) and humic acid are shown in table 1. The selected chemical and physical characteristics of studied soils indicated to nitrogen loss from these soils as it was shown by Terman & Hunt (1964), Al-Kanani et al (1990) and Theiab (1996). Total organic carbon, carboxylic, phenolic groups and total acidity of humic acid were within the range reported by other authors (Stevenson 1994; Al-Tamimi 1998; Tan 2003). The values of carboxylic, phenolic and total acidity of humic acid indicates the ability of humic acid to adsorb more cations and form organo-mineral complexes as shown by above mentioned authors.

Daily loss of ammonia (NH_3) is shown in table 2 & 3. Ammonia loss started a three days after incubation for urea (probably due to delay in urea hydrolysis). The maximum ammonia loss for both soils was occurred on the third day. A rapid loss of ammonia from urea alone was probably due to increased of pH at the soil microsite as urea hydrolysis leads to consumption of hydrogen ions (H^+) from the soil solution (Rosliza et al 2009), Removal of more H^+ associated with low buffering capacity of Zubair (loamy sand) soil, increased the soil pH and enhanced more formation of NH_4^+ over NH_3 as compared with Abul-Khasseb (silty clay) soil. The total amount of ammonia lost at the end of the incubation period (5, 10, 20, 30, 40 and 60 days) as a percentage of urea–N in the studied soils were (17.9, 7.64, 5.73, 4.20, 2.30 and 1.91 %), (36.16, 16.44, 11.84, 1.32, 0.00, 0.00 %) respectively. A similar observation was shown by Ahmed et al (2006) who showed ammonia loss two days after incubation of urea, while Rosliza et al (2009) showed ammonia loss started a day after incubation of urea, the differences of these results are due to differences of soils chemical and physical characteristics.

Increasing of humic acid rates (0, 2.5, 5.0 g kg^{-1} soil) significantly reduced ammonia loss compared with urea alone in both studied soils (Table 2 & 3). The finding agree with the works of Siva et al (1999), Ahmed et al (2006) and Rosliza et al (2009) who was also found a reduction in NH_3 loss when urea was mixed with peat or humic acid. Above mentioned authors found that when urea was mixed with peat or humic acid, the acidic products lowered microsite pH, reduced urea hydrolysis and caused a reduction in ammonia loss. Ammonia loss reduction was 44.20 and 68.35 % for Abul-Khasseb soil and 10.20 and 28.10 % for Zubair soil at the rates of 2.5 and 5.0 g humic acid kg^{-1} soil as compared control treatment (Table 2 and 3). The total acidity (CEC) provided by hymic acid 750 Cmol kg^{-1} (Table 1) may have contributed to ammonia loss reduction. The negative sites due to ionization of carboxylic (COOH) and phenolic (OH) might have improved ammonium (NH_4^+) retention hence reduction in N loss (Lethbridy & Burns 1976). These negative charges could develop with increasing of soil pH values of the studied soils (Table 1).

Table 2

Amounts of ammonia loss over six periods of incubation in Abul-Khasseb soil

HA rates g kg^{-1} soil	*N-rates* mg kg^{-1} soil	*NH_3 (%)*						*Cumulative NH_3 %*
		3 d	10 d	20 d	30 d	40 d	60 d	
	0	17.19	7.64	5.73	4.20	2.30	1.91	38.2
0	60	23.27	10.34	7.75	5.15	3.10	2.60	51.70
	120	31.95	14.45	11.10	7.57	4.13	3.44	72.34
	0	10.68	4.96	3.48	2.23	1.24	0.75	23.34
2.5	60	13.34	5.89	4.34	2.80	1.55	1.24	29.16
	120	18.40	7.70	5.56	3.42	1.72	1.28	38.08
	0	6.00	2.83	1.94	1.20	0.60	0.45	13.02
5.0	60	7.55	3.24	2.52	1.62	0.72	0.54	16.19
	120	10.55	4.31	3.36	2.04	1.29	0.60	22.15

HA – humic acid; d – days.

Table 3

Amounts of ammonia loss over six periods of incubation in Zubair soil

HA rates g kg^{-1} soil	*N-rates* mg kg^{-1} soil	*NH_3 (%)*						*Cumulative NH_3 %*
		3 d	10 d	20 d	30 d	40 d	60 d	
	0	36.16	16.44	111.84	1.32	0.0	0.0	65.76
0	60	47.18	21.91	16.00	0.84	0.0	0.0	85.93
	120	50.92	25.00	18.26	1.92	0.0	0.0	96.10
	0	32.46	14.43	10.51	1.20	0.60	0.0	59.70
2.5	60	42.04	18.68	12.84	1.55	0.78	0.0	75.89
	120	46.22	19.18	17.44	1.65	1.31	0.90	86.70
	0	26.73	10.79	8.22	2.57	1.03	0.60	49.94
5.0	60	32.40	13.08	9.35	3.12	1.56	0.40	59.91
	120	35.93	14.10	10.57	3.52	2.82	0.69	67.63

HA – humic acid; d – days.

Increasing nitrogen rates (0, 60 and 120 mg N kg^{-1} soil) significantly increased ammonia loss by volatilization process in both studied soils. The increase in nitrogen loss was 30.18, 77.83 % in Abul-Khasseb soil and 26.41, 42.77 % in Zubair soil at rates 60 and 120 mg N kg $^{-1}$ soil as compared with control treatment respectively (Table 2 & 3). As the concentration of ammonium ions in the soil solution increased by addition of nitrogen the urea increased the ammonia volatilization. These results are agreed with those reported by Stumpe et al (1984), Theiab (1996) and Ahmed et al (2006).

The treatments of nitrogen rates with humic acid rates significantly reduced ammonia loss compared with urea without humic acid (Table 2 and 3). The reduction of ammonia loss was highly related to the highest retention of ammonium ion by functional groups (carboxylic and phenolic) of humic acid besides low soil pH obtained by mixing humic acid with urea treatments. Functional groups effectively replaced the remove H^+ ion during urea hydrolysis thus aiding in buffering the soil pH from increasing sharply and showing down the rate of ammonia volatilization (Rosliza et al 2009), this observation was agreed with our results, there was no significant differences in soil pH with increasing rates of humic acids and urea in Zubair soil as compared with Abul-Khasseb soil (Table 4 & 5).

Table 4

Effect of humic acid and nitrogen rates on soil pH, exchangeable ammonium and nitrate over 60 days of incubation in Abul-Khasseb soil

HA rates g kg^{-1} soil	*N-rates mg kg^{-1} soil*	*pH (H_2O)*	*NH_4^+*	*NO_3^-*
			mg kg^{-1} soil	
0	0	7.80	35.60	12.10
	60	8.00	37.45	12.90
	120	8.10	39.60	14.00
2.5	0	7.60	36.15	13.25
	60	7.85	39.20	14.63
	120	7.95	41.38	17.00
5.0	0	7.50	37.10	15.40
	60	7.40	40.45	17.00
	120	7.30	46.25	19.85

HA – humic acid.

Table 5

Effect of humic acid and nitrogen rates on soil pH, exchangeable ammonium and nitate over 60 days of incubation in Zubair soil

HA rates g kg^{-1} soil	*N - rates mg kg^{-1} soil*	*pH (H_2O)*	*NH_4^+*	*NO_3^-*
			mg kg^{-1} soil	
0	0	8.10	7.10	3.50
	60	8.15	7.52	3.90
	120	8.25	7.76	4.13
2.5	0	8.00	7.25	3.60
	60	8.05	7.90	4.30
	120	7.85	8.50	4.90
5.0	0	7.90	7.55	3.75
	60	7.85	9.35	5.50
	120	7.70	11.25	7.35

HA – humic acid.

There was significant accumulation of exchangeable NH_4^+ for all the mixtures of humic acid with urea compared to urea alone (Table 4 & 5). This differences can be explained based on the fat in this present study, the addition of humic acid might have improved the soil $NH4^+$ retention ability and hence favoring adsorption of NH_4^+ over rapid nitrification from excess of NO_3^-. This observation was more clear in Abul-Khasseb soil than in Zubair soil, this observation in NH_4^+ retention can be used in improving urea efficiency in calcareous soils because a soil with high level of NH_4^+ without effective retention does not guaranties plant N use efficiency. This is because plant N use efficiency can be decreased by the biological transformation of NH_4^+ to NO_3^- (Brady & Weil 2002). Although both NH_4^+ and NO_3^- are plant available forms, NO_3^- is more mobile than NH_4^+ thus making it more susceptible to leaching loses particularly in area of rainfall and sandy soils.

Conclusions. We demonstrated in a laboratory study that ammonia volatilization can be significantly reduced using humic acid over urea alone, because of its ability to benefit formation of NH_4^+ over NH_3. It could be an economical efficient, the easiest and practical way in controlling N loss as well as reducing environmental pollution.

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