

Some Soil Factors Affecting Air Pollution by Ammonia Volatilization from Urea Fertilizer

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AMMONIA volatilization from urea reduces nitrogen fertilizer efficiency of crops and increased air pollution. Some soil factors such as clay percent, calcium carbonate content, moisture regime and organic matter content were studied in two of laboratory incubation experiments under aerobic conditions at $20 \pm 2^\circ$. Soil samples were collected from Qalubia Governorate, Ismailia Governorate and Alexandria Governorate which represented clay loam, sandy and calcareous soils, respectively. Ammonia volatilization losses from urea reached 14.4, 26.7 and 32.6% of the applied urea fertilizer to clay loam, sandy and calcareous soils, respectively. Whereas, ammonia volatilization increased as a result of increasing calcium carbonate content in the soil (calcareous soil) by about 2.3, and 1.2 times compared to clay loam and sandy soils, respectively. Moreover, the increases of ammonia volatilization from soil at 50% of water holding capacity were 38, 76 and 88 % relative to those found at 100 % water holding capacity after three weeks of applied urea to the investigated soils, respectively. Also, application of cattle manure at rates of 2 and 5% decreased the amount of NH_3 volatilization from calcareous soil by about 43.1 and 53.6 % at full water holding capacity. The concentration of NH_4^+ in the soil solution increased due to application of urea fertilizer particularly when cattle manure and clay content were increased along with low water content in soil. Such increases recorded 57, 135 and 165% at the end of experiment (21 days) at low moisture in clay loam, sandy and calcareous soils, respectively. On the other hand, the values of nitrate concentration decreased with increasing water content in the different soils.

So, the results showed that soil pH, water content and organic matter content are major factors influencing ammonia losses from soils compared with the other studied factors.

Keywords: Ammonia, Volatilization, Urea, Clay content, Organic matter, Calcium carbonate, Moisture regime

Most agricultural soils are deficient in nitrogen for the growth of crops. This deficiency can be overcome by application of fertilizers, but fertilizer nitrogen is not always used efficiently. Because of the relatively low manufacturing cost of urea, and its low transportation cost per unit of nitrogen, there has been a widespread move to urea as the major form of nitrogen produced and used. However, there is concern about the efficiency of using urea-nitrogen for agricultural crops, especially in flooded soil. In general, gaseous emissions of

nitrogen via ammonia (NH_3) volatilization and denitrification have been identified as the dominant mechanisms of fertilizer nitrogen loss in many different agricultural systems (Peoples *et al.*, 1995). Large losses of NH_3 from applied fertilizer have been detected from soil, floodwater, and irrigation water in many agroecosystems. Other variables which influence NH_3 volatilization include the pH-buffer capacity and cation exchange capacity of the soil, levels of urease activity, soil moisture, nitrification rate, and the presence of plants or plant residues (Freney & Black, 1988). Losses of NH_3 measured from different upland and lowland cropping systems have ranged from negligible amounts up to > 50% of the fertilizer N applied, depending upon fertilizer application and environmental conditions (Bacon *et al.*, 1986; Keller & Mengel, 1986; Black *et al.*, 1989 and Freney & Denmead, 1992). Some of the most important factors regulating NH_3 loss are the concentration of $\text{NH}_4^+\text{-N}$, the temperature, wind speed and the pH of the soil solution or irrigation water, since all these variables markedly affect the partial pressure of NH_3 . (Denmead *et al.*, 1982 and Fillery *et al.*, 1984). Levels of N loss influenced by fertilizer composition, and the rate or timing of application (Strong *et al.*, 1992 and Diekmann *et al.*, 1993).

This investigation aimed to study the effect of clay content, calcium carbonate percent, water and organic matter contents on ammonia volatilization from the soil under aerobic conditions.

Material and Methods

Surface soil samples (0-15cm) were collected from three different sites; the first sample was taken from Agricultural Experimental Station of the Faculty of Agriculture, Ain Shams University, Qalubia Governorate. The second sample was taken from Agricultural Research Station, Ismailia Governorate and the last one was taken from Burg El-Arab, Alexandria Governorate, Egypt (Table 1). The soil samples were air dried, ground and passed through a 2mm sieve. Two incubation experiments were conducted to study the effect of clay content, CaCO_3 , water and organic matter contents on hydrolysis of urea and ammonia volatilization under aerobic conditions at $20 \pm 2^\circ$. The details are as follows:

A. The objective of the first experiment was to study the effect of clay content and initial soil pH on hydrolysis and ammonia volatilization of urea at 50 and 100% of water holding capacity. The nitrogen fertilizer was applied to the surface of the soil at a rate of 200 kg fed^{-1} (0.2 g kg^{-1} soil) as urea.

B. The objective of the second experiment was to study the effect of water content and cattle manure application to calcareous soil on hydrolysis and ammonia volatilization of urea. The cattle manure was applied at three levels, *i.e.*, 0, 2 and 5 % by weight of soil. Nitrogen of urea application rate and moisture content were as previously mentioned in the first experiment. The organic manure characterized by having a total nitrogen of 15.9 gkg^{-1} , organic carbon of 258 gkg^{-1} , nitrate of 13.42 gkg^{-1} , ammonium of 3.47 gkg^{-1} and C: N ratio of 16:1.

TABLE 1. Some physical and chemical properties of the soils used.

Property	Qalubia Soil	Ismailia soil	Burg El - Arab soil
Particle size distribution (%)			
Sand	29.98	88.71	43.79
Silt	36.10	7.12	25.99
Clay	33.92	4.17	30.22
Texture class	Clay loam	Sand	Clay loam
E_c ($dS.m^{-1}$)	0.91	0.48	1.60
pH 1:2.5	7.45	7.86	8.20
O.M (%)	1.12	0.50	0.73
Total $CaCO_3$ (%)	4.19	2.60	31.00
Active $CaCO_3$ (%)	0.53	0.24	12.55
Field capacity (%)	43.25	18.29	39.28
Holding capacity	88.25	41.17	82.46
CEC ($cmol.Kg^{-1}$ soil)	25.34	3.21	20.41
NH_4^+ ($mg.Kg^{-1}$ soil)	28.15	9.76	19.60
NO_3^- ($mg.Kg^{-1}$ soil)	19.24	4.58	11.23

In the two experiments, 5kg portions of soil samples were placed in spherical flask to allow an air draft to help in collecting volatilized ammonia. The volatilized NH_3 collection system (Fig. 1) used in this study was based upon equipment designed as modified by Abou Seeda (1997).

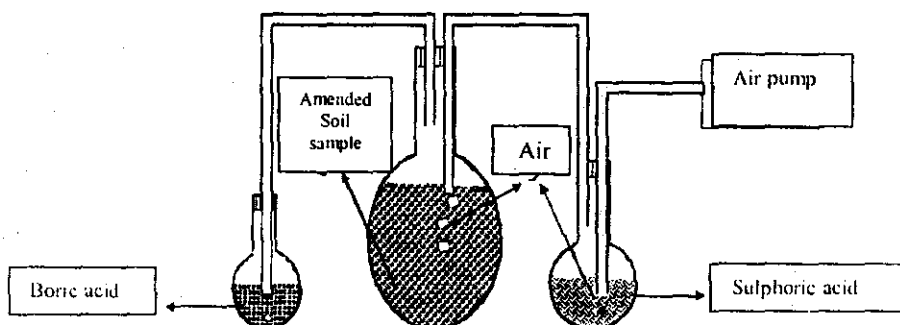


Fig. 1. Schematic diagram for volatilization apparatus.

Representative tested soil samples were taken from spherical flask at zero time and daily for 21 days of incubation. The collected samples were air dried, crushed, sieved through a 2-mm sieve and stored for nitrate and ammonium determinations according to Keeney & Nelson (1982). Some physical and chemical characteristics of the studied soils and manure were determined by standard procedures (Black, 1965 and Jackson, 1973).

Results and Discussion

Ammonia volatilization

As for the concentration of urea in soil, data presented in Table 2 show that the ammonia volatilization rates were generally different from soil to another and it gradually increased with time following urea application to the soil. This finding was pronounced in sandy soil (Ismailia soil) compared to the other studied soils, whereas the highest amount of the applied urea loss (6.97% from the added urea) was found after 9 days from urea application to sandy soil at 50% of water holding capacity while at 100% of water holding capacity, the ammonium volatilization rate was somewhat reduced to about 3.88% from the added urea. It is clear also that the highest ammonia emission from clay loam soil was found after 12 days following urea addition, where its value reached 3.87 and 2.41% of the applied urea from Qalubia soil and 8.12 and 5.38% from Burg El-Arab soil at 50 and 100 % of water holding capacity, respectively. This result indicates that increasing the water content of the soil led to increase the movement of urea into soil and cause it to disperse and to be less concentrated. Humphreys *et al.* (1988) reported that flood irrigation has been used to disperse the granules of surface applied urea and wash the solubilized urea into the soil. When this technique was used to apply urea for a subsequently flooded rice crop, no ammonia was lost to the atmosphere. In this respect, after either 9 or 12 days from urea application to the sandy soil or clay loam soils, the loss of ammonia was reduced thereafter until the end of experiment (21 days). So that by the end of study, 14.3, 26.68 and 32.6% of the urea had been lost at 50% of water holding capacity for Qalubia, Ismailia and Burg El-Arab soils (clay loam, sandy and calcareous soils), respectively. This finding was less observed at 100% of water holding capacity as above mentioned. The total loss probably would not have exceeded 14.3 to 32.6% of the applied urea to the investigated soils. These results could be attributed to the consumption of oxygen by aerobic microbes. These results are in good agreement with those obtained by Zhu (1992) who stated that in flooded rice, NH_3 volatilization could account for 20 % to more than of the total N lost from fertilizer sources. In other words, soil water content has the greatest effect on the rate of urea hydrolysis and this rate does not change greatly at water contents that are readily available to plants. These results are accordance with those obtained by Al-Kanai (1991) who indicated that hydrolysis of urea is promoted under conditions of elevated soil moisture (as already mentioned), which can then enhance evaporation losses as NH_3 and CO_2 .

Concerning the effect of soil pH prior to adding urea, it's clear that soils under investigation vary in their ability to supply hydrogen ions, which are released from soil clays and organic matter per unit rise in pH. In general, soils with more hydrogen ion buffering have more clay and organic matter. So, sandy soil, usually low in both, is typically very poorly buffered. The result is typically a higher pH when urea is applied to sandy soil. Data given in Table 2, reveal that calcareous soil (pH 8.2) had the least hydrogen ion buffering. So, the ammonia loss was greater from it, such values increased by about 2.3 and 1.2 times as compared to clay loam soil (pH 7.45) and sandy one (pH 7.86). In other words, the higher pH

allowed a greater proportion of the ammonia form, which resulted in more loss. In turn, the Qalubia soil (clay loam soil) with most hydrogen ion buffering had the lowest pH (7.45) and also the least ammonia loss. These results are in harmony with those obtained by Tisdale *et al.* (1985) who reported that ammonia volatilization is significant only if the soil surface pH value is greater than 7 where the urea is applied. These conditions occur in calcareous soils or where the urea breakdown creates alkaline conditions near the fertilizer particle.

TABLE 2. Ammonia volatilization rates (mg Kg⁻¹ soil) from urea fertilizer in different soils.

Days after application	Qalubia (Clay loam) soil		Ismalia (Sandy) soil		Burg El-Arab (Calcareous) soil	
	50% HC	100%HC	50% HC	100%HC	50% HC	100%HC
	mg.Kg ⁻¹ soil					
3	0.77	0.52	2.41	1.31	2.28	1.11
6	1.46	0.86	3.65	2.19	5.09	3.39
9	2.41	1.72	13.94	7.77	7.37	4.56
12	7.57	4.82	11.53	6.94	16.43	10.76
15	6.45	3.96	8.47	5.22	13.04	6.25
18	6.02	3.27	7.88	5.22	11.93	5.3
21	4.04	2.67	5.48	3.02	9.06	8.53
Sum	28.72	17.82	53.36	31.67	65.20	39.90

* HC= Water holding capacity.

Data in Table 3, indicate that increasing the application of organic manure rates up to 2 and 5% reduced ammonia volatilization by about 43.1 and 53.6, respectively relative to the control treatment (without cattle manure addition) at 100 % of water holding capacity. This result may be attributed to increasing the presence of urease enzyme in organic manure consequently promoted the form of ammonium ions which can attach soil exchange sites thus slowing or stopped the reactions leading to ammonium emission from the manured treatment particularly when it's applied at the high application rate (5%). Rodhe *et al.* (1996) declared that in addition to chemical fertilizer sources, NH₃ volatilization losses from organic fertilizer can be substantial. But irrigation immediately after spreading waste may significantly reduce NH₃ emission from the manured plots. They also mentioned that the hydrolysis of applied urea increased with increasing urease enzyme in the soil which highly correlated with the amount of both soil clays and soil organic matter.

In this concern, McInnes *et al.* (1986) stated that the concentration of urease enzyme was found to be 20 to 30 times higher in crop residue than underlying. Therefore, urea placed directly on organic manure can rapidly form ammonium if temperature and moisture conditions are conducive to urea hydrolysis.

TABLE 3. Ammonia volatilized (mg Kg⁻¹ soil) from calcareous soil as a function of urea fertilizer, organic manure and moisture regime.

Days after application	0 % cattle manure		2 % cattle manure		5 % cattle manure	
	50%HC*	100%HC	50%HC	100%HC	50%HC	100%HC
	mg.kg ⁻¹ urea fertilizer					
3	2.28	1.11	2.11	0.69	2.40	0.51
6	5.09	3.39	3.75	1.16	2.94	1.55
9	7.37	4.56	5.60	2.33	3.20	2.07
12	16.43	10.76	6.55	4.46	3.74	3.88
15	13.04	6.25	7.03	5.42	5.62	4.91
18	11.93	5.30	8.88	4.38	5.39	2.84
21	9.06	8.53	8.34	4.26	5.07	2.76
Sum	65.20	39.9	42.26	22.7	28.36	18.52

* HC= Water holding capacity.

Transformations of urea in soils

The changes of NH₄⁺ and NO₃⁻ contents in clay loam, sandy and calcareous soils during the period of 21 days are recorded in Table 4. The obtained data showed that ammonium and nitrate concentrations in different soils appeared steadily increasing with time up to 9, 12 and 15 days following urea application to clay loam, sandy and calcareous soils, respectively. While after 15 days from incubation, the ammonium and nitrate concentrations decreased in different soils with time. On the other hand, the rate of nitrate concentration was higher than the rate of ammonium concentration in both clay loam and sandy soils at 50% of water holding capacity. While at 100% of water holding capacity, the opposite trend was attained. This of course is a result of urea hydrolysis and nitrification process that occurs in such conditions. It is worth to notice that transformation of the added urea took an opposite pattern in calcareous soil at both 50 and 100% of water holding capacity. However, soil factors that strongly influence denitrification are oxygen, nitrate concentration, pH, temperature and organic carbon (Peoples *et al.*, 1995). Denitrification occurs in soil aggregates and anaerobic microsites which are heterogeneous by distributed in the soil (Parkin, 1987); or only when the soil water content is 76% of the air-jelled pore space (Linn & Doran, 1984). The obtained results in Table 4, confirmed the theory that nitrate is the prevailing form of nitrogen in the soil. Addition of urea fertilizer associated with increasing water content in different soils seemed to have retarding action on the nitrification process. The values of NH₄⁺ are bit higher in the treatment with low water content compared to high water percent in the soil. This finding is taking an opposite trend for nitrate. This phenomenon is well known and sometimes raises the question about the fate of nitrate in soil. It may be ascribed to either immobilization by soil microorganisms or the loss of reduced nitrate forms. It should be noted that although the current experiment was conducted under aerobic conditions, there are locations where anaerobic conditions might prevail especially in clay loam soil (Qalubia soil). Under such

circumstances, possible nitrate reduction to various nitrogen oxides and even nitrogen gases and consequently their volatilization. Similar results were obtained by Norman *et al.* (1987).

TABLE 4. Nitrate and ammonium contents (mg Kg⁻¹soil) as affected by urea fertilizer hydrolysis in different soils.

Days after application	Clay soil				Sand soil				Calcareous soil			
	50%HC		100%HC		50%HC		100%HC		50%HC		100%HC	
	NH ₄ ⁺	NO ₃ ⁻	NH ₄ ⁺	NO ₃ ⁻	NH ₄ ⁺	NO ₃ ⁻	NH ₄ ⁺	NO ₃ ⁻	NH ₄ ⁺	NO ₃ ⁻	NH ₄ ⁺	NO ₃ ⁻
	mg. Kg ⁻¹ soil.											
3	2.43	1.71	204	145	0.52	0.24	1.27	0.17	1.73	0.71	4.97	0.49
6	2.73	10.75	12.42	2.44	3.36	6.94	7.68	3.80	4.08	3.08	7.35	2.05
9	6.50	13.83	15.76	17.02	7.33	10.16	18.33	8.37	4.33	3.62	10.17	2.41
12	14.94	22.56	23.61	15.34	6.97	9.70	15.07	7.92	4.90	4.58	15.42	3.04
15	14.55	21.44	22.45	13.40	5.44	11.28	13.31	6.13	7.10	7.60	19.49	4.48
18	14.12	18.20	17.48	10.73	4.52	9.37	11.03	5.13	6.38	5.68	17.57	3.36
21	13.72	15.05	14.47	8.21	4.16	8.67	9.51	4.80	5.40	4.97	14.83	3.32
Sum	68.99	103.54	108.23	68.59	32.30	56.36	76.20	36.32	33.92	30.24	99.80	19.15

*HC= Water holding capacity

Concerning the effect of organic manure under different water contents on transformation of urea in calcareous soil, data presented in Table 5, show that the relative increase in both NH₄⁺ and NO₃⁻ was noticed as a result of organic manure application, regardless of soil water content. Such increase reached a maximum rate after 12 days from urea application thereafter it gradually decreased. The total increase at the end of experiment (21 days) when 2 and 5% organic manures were used at 50% of water holding capacity were 75.4 and 72.9% for NH₄⁺ and 310 and 364% for NO₃⁻, as compared to the control treatment (without cattle manure addition). These values represented about 29.5% of total applied urea lost as NH₄⁺ and from 44 to 50% as NO₃⁻. These results confirmed the role of organic matter in reducing NH₃ volatilization from urea due to supplying protons and electrons for the reduction process. It is also clear that under 100% of water holding capacity, the total NH₄⁺ ions were more than NO₃⁻ ones at both 2 and 5% cattle manure application rate but the obtained values were still higher than the corresponding ones obtained for the control treatment. This indicates that organic manure plays a vital role in increasing the nitrogen availability through microorganisms activities, besides decreasing nitrogen losses by leaching and volatilization (Mary *et al.*, 1996). Moreover, urea is holding on the soil colloids by weak forces giving a better chance for hydrolysis and nitrification.

TABLE 5. Nitrate and ammonium contents (mg Kg⁻¹ soil) in calcareous soil as affected by urea fertilizer hydrolysis as a function of cattle manure and moisture regime.

Days after application	0 % cattle manure				2 % cattle manure				5 % cattle manure			
	50%HC*		100%HC		50%HC		100%HC		50%HC		100%HC	
	NH ₄ ⁺	NO ₃ ⁻	NH ₄ ⁺	NO ₃ ⁻	NH ₄ ⁺	NO ₃ ⁻	NH ₄ ⁺	NO ₃ ⁻	NH ₄ ⁺	NO ₃ ⁻	NH ₄ ⁺	NO ₃ ⁻
3	1.73	0.71	4.97	0.49	2.10	1.47	2.46	0.36	0.95	0.42	2.40	0.82
6	4.08	3.08	7.35	2.05	2.35	9.21	15.31	1.35	6.11	12.38	15.30	4.23
9	4.33	3.62	10.17	2.41	5.60	11.86	18.80	4.53	7.56	15.47	18.87	5.35
12	7.10	7.60	19.49	4.48	12.89	19.34	27.81	11.44	13.30	18.13	33.23	9.33
15	6.38	5.68	17.57	3.36	12.55	18.38	26.85	11.14	12.65	17.31	32.05	8.83
18	5.40	4.97	14.83	3.32	12.17	15.60	21.04	9.86	9.87	20.12	24.88	6.84
21	4.90	4.58	15.42	3.04	11.82	12.90	17.46	8.97	8.22	16.71	20.86	5.72
Sum	33.92	30.24	89.80	19.15	59.48	88.76	129.73	47.65	58.66	100.54	147.59	41.12

* HC= Water holding capacity.

From the above mentioned results, it can be concluded that soil water content, soil texture, soil pH and organic matter content played dominant roles in controlling the amount of ammonia loss from surface applied urea. Moreover, the management of nitrogen is of concern to farmers engaged in agricultural production and to researchers and environmentalists concerned with the effects of the lost nitrogen on climatic change. This aimed also at increasing the efficiency of nitrogen fertilizer use by crops and provides an incentive for reducing the impact on the environment.

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(Received 3/2004)

تأثير بعض عوامل التربة على تحلل اليوريا وتلوث الهواء بالأمونيا

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يحدث مشاكل التسميد باليوريا هو فقد الامونيا بالتطاير مما يؤدي إلى زيادة تلوث الهواء الجوي ويقلل من كفاءة استخدامها كسماد نيتروجيني. لذلك تم إجراء تجربتين في المعمل تحت الظروف الهوائية عند درجة حرارة 20 ± 2 درجة مئوية على ثلاث أراضى من مناطق مختلفة (أرض طينية من محافظة القليوبية ، أرض رملية من محافظة الإسماعيلية، أرض جيرية من محافظة الاسكندرية) بهدف دراسة تأثير كلا من نسبة الطين، كربونات الكالسيوم، محتوى التربة من الرطوبة ، المادة العضوية على مدى تحلل اليوريا وتلوث الهواء الجوي بالامونيا.

لوضحت النتائج مايلي:

وصلت كمية الامونيا المفقودة نتيجة تحلل اليوريا إلى 14.4، 26.7، 32.6٪ من كمية اليوريا المضافة إلى الأرض الطينية ، الرملية والجيرية على الترتيب، نلت للنتائج على أن إضافة سماد اليوريا إلى الأراضي الجيرية أدى إلى زيادة للكمية المفقودة من الامونيا بمقدار 2.3، 1.2 مرة مقارنة بالكمية المفقودة من الأراضي الطينية والرملية على الترتيب. وبدراسة تأثير الرطوبة على كمية الامونيا المفقودة بالتطاير عند مستوى رطوبة 50٪ من السعة التشبعية العظمى قد وصلت إلى 38، 26، 88٪ مقارنة بالمفقودة عند محتوى رطوبي 100٪ من السعة التشبعية العظمى بعد ثلاث أسابيع من بداية التجربة من الأرض الطينية ، الرملية، الجيرية على الترتيب.

وتضح من الدراسة أيضا أن إضافة السماد العضوي إلى الأراضي الجيرية بنسبة 20.5٪ قد أدى إلى خفض تطاير الامونيا إلى 43.1، 53.6٪ عند نسبة رطوبة 100٪ من السعة التشبعية العظمى على الترتيب.

تعمتنت النتائج السابق ذكرها على محتوى التربة من النيتروجين الامونيومي والنتراتي فقد وجد أن تركيز النيتروجين الامونيومي قد زاد بزيادة كلا من المادة العضوية، نسبة الطين وانخفاض محتوى رطوبة التربة وهذه الزيادة قد وصلت إلى 57، 135، 165٪ بعد 21 يوم من إضافة سماد اليوريا عند مستوى رطوبة 50٪ من السعة التشبعية العظمى في الأرض الطينية ، الرملية و الجيرية على الترتيب وعلى العكس من ذلك فقد انخفض تركيز النتترات مع زيادة المحتوى الرطوبي في جميع الأراضي تحت الدراسة.

أوضحت النتائج أن درجة حموضة التربة pH ، نسبة المسادة العضوية و نسبة الرطوبة تعتبر من العوامل الأساسية التي تؤثر على فقد الامونيا عند استخدام اليوريا نثرا على سطح التربة مقارنة بقيالي العوامل تحت الدراسة.

ولهذا توصي للدراسة بتوخي الحذر عند استخدام سماد اليوريا في الأراضي الرملية (خفيفة التوام) وذات المحتوى العالي من كربونات الكالسيوم وان كان لابد من استخدامها فيجب الاهتمام بإضافة السماد العضوي مع تقارب فترات الري وعدم وضع السماد دفعة واحدة نثرا على سطح التربة.