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PN-AAT-952

92592

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TDY REPORT

TECHNICAL

VOLATILIZATION AND DENITRIFICATION LOSSES OF UREA-N APPLIED TO EGYPTIAN SOILS

BY

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EMCIP Publication No. 55

by

Consortium for International Development

Published: February, 1983

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ACKNOWLEDGEMENTS

The author wishes to thank Dr. B.C. Williams for his support during the course of the study. I would also extend my appreciation to Dr. Virgil Smail for his efforts in establishing an acceptable field design and assisting in the field management work.

Dr. Nabil Alaa El-Din, provided the facilities in Soil Microbiology and also made several helpful technical suggestions. I am indebted to him. Dr. Mohamed Eid Abd-El-Meguid proved to be an extremely capable co-worker during all phases of the study. His expertise in Biochemistry and Microbiology contributed greatly to the success of the study.

Technical assistance provided by Mr. Aly Abd-El-Hafiz Ali, Mr. Fathi Tewfik Mechaiel, Mr. Hamdy Ahmed Anwar Mustafa was indeed appreciated.

Our drivers for the field work Mr. Yehia Hassan and Mr. Magid Maher also assisted in taking fields samples and became an integral part of our research team. They all deserve to be commended for their efforts.

I also appreciated the administrative support provided by directors of the Research Extension Centers, ARC - Giza, by the Program Leader for Wheat and Barley and Chief of Party, EMCIP; and Deputy Chief of Party, EMCIP.

I would also express appreciation to the secretaries and my wife Margaret for help in the preparation of this report.

TDY REPORT

Dr. C.M. Gilmour

Introduction

The primary objective of my TDY visit to Egypt has been to develop an experimental methodology suitable for the determination of volatilization (NH_3) and denitrification (N_2O, NO) losses with urea fertilizer as the source of nitrogen. During my first week (October 2 - 7) I was introduced to the EMCIP staff and a number of our Egyptian colleagues. After considerable discussion a work plan was developed.

Work Plan

Study Location: ARC - GIZA, GEMMEIZA and SIDS Research/Extension Centers

Objectives

A. Laboratory Studies

1. To calibrate the chemical assay methods for the determination of NH_3 and the detection of No_x nitrogen.

2. To conduct laboratory experiments designed to provide preliminary data on volatilization and nitrogen losses.

B. Field Studies

1. To determine the loss of urea nitrogen under different methods of fertilizer placement (surface, incorporated and drilled).

2. To evaluate the effect of irrigation timing on soil nitrogen losses.

C. Report

It is expected that both the laboratory and field data will be used to modify or support current recommendations for the use of urea as a nitrogen fertilizer. In addition, it is hoped that the laboratory tests for volatilization and denitrification losses will compare favorably with the data obtained under field conditions.

If such proves to be the case then the less expensive and time consuming laboratory tests can become predictive for large field areas.

Facilities and Personnel

After discussions with Dr. Nabil Alaa El Din it was decided that the ARC Soil Microbiology Laboratory would be used as the central assay laboratory. In addition, Dr. Mohamed Eid Abd El Meguid would serve as the primary Egyptian co-investigator for the study. In the field Dr. Boyce Williams, Dr. Virgil Smail, Mr. Sayed Khalik (Sids), Dr. Rashad Abou El-Enein, Dr. Abd Maboud Shaty, Dr. Fathi Farag (Gemmeiza) and Dr. Abdel Salam Gomaa were directly involved in the field design. Because of his earlier studies and valuable experience in the area of volatilization losses, Dr. M. Riyad Hamissa served as a consultant. Technical assistance was provided by Mr. Aly abd El Hafiz Ali, Mr. Fathi Tewfik Mechaiel and Mr. Hamdy Ahmed Anbar Mustafa.

Historical

In early classical review articles Allison (1955, 1965) called attention to the difficulty in attaining acceptable soil-nitrogen balances and, in doing so, emphasized the vast interlocking system of nitrogen loss pathways. Various studies (Allison et al., 1962; Cady and Bartholomew, 1961; Clark and Beard, 1960) conducted under laboratory conditions showed that, when non-excessive rates of inorganic nitrogen fertilizer were used and the system maintained in the aerobic state, little nitrogen was lost at optimum moisture levels. Poor recoveries attributable to ammonia volatilization were normally not encountered. However, the volatilization pathway is now given greater attention primarily because of increased use of ammoniacal nitrogen sources and the extensive use of urea. Meyer et al., 1961; Burton and Jackson, 1962; Harding et al, 1963 showed that, when urea is applied as a top dressing on grasses or even bare soil, ammonia losses may range from 15-25% of the input urea nitrogen. Broadbent et al, 1958, stressed the importance of temperature in respect to rate of urea hydrolysis. Hamissa and Shawaibi, 1962, reported less than 1% ammonia loss at a soil temperature of 6°C and a 4.2% loss at 31°C. These authors also observed that relatively low volatilization values were obtained on the acid side of the pH scale (pH 6.2) and that only a 0.02%

loss was shown when the urea fertilizer was placed 2 cm below the surface. These and other studies make clear that the rate and extent of ammonia volatilization increase with soil pH, fertilizer concentration, decrease in moisture content and increase in soil temperature.

Mortland, 1958, presented a classical review of the fate of ammonium ion reactions in soils. The ammonium ion may be chemically absorbed by clay minerals and organic matter, physically fixed by soil colloids or it may be in the soil solution. Of special interest is the fact that losses are inversely related to soil exchange capacity which places special significance on the nature and amount of clay minerals in the soil.

Studies by Fenn et al., 1973, 1976, 1982, again called attention to the volatilization losses encountered with surface applied urea on calcareous soils. Unfortunately these studies were carried out at relatively high soil temperatures and thereby maximized the losses. However, Fenn et al., 1982, did present an interesting approach to effect decreases in volatilization losses. These authors offered the hypothesis that NH_4^+, Na^+ or K^+ indirectly decrease NH_4^+ loss by replacing Ca^{++} on the exchange sites allowing precipitation of Ca^{++} as $CaCO_3$. Thus, the concomitant use of urea and other fertilizers (NH_4NO_3, NH_4Cl, KNO_3) would decrease losses with surface-applied urea. Their data support this recommendation.

The above brief comments on past studies were not intended to give full coverage of the literature on soil nitrogen losses but rather to focus on key aspects of the volatilization process particularly in respect to mediating factors. It is clear that temperature. pH, CEC, fertilizer concentration and moisture level are the primary factors which determine the process rate. Any one factor can markedly increase or decrease volatilization losses and consequently cannot be ignored.

Denitrification is a biological process resulting in the reduction of NO_3^- - N to gaseous N_2O, NO and N_2. It should be differentiated from the reduction of NO_3^- to NO_2^- which can be termed nitrate reduction. In both cases NO_3^- is being used as the terminal acceptor of hydrogen during the oxidation of carbohydrate to CO_2 Anaerobic conditions are required for the complete reduction of NO_3^- to N_2O and N_2, whereas NO_3^- can be reduced to NO_2^- under aerobic conditions (McGarity et al, 1958; Gilmour

et al., 1964). Many other investigators have shown that the partial pressure of oxygen, the dissolved oxygen content of the soil solution and the presence of readily oxidizable carbon represent the key mediating factors for denitrification (Allison et al., 1960; Cady and Bartholomew, 1961; Woldendrop, 1962). Under field conditions denitrification losses can be extensive at high moisture levels provided that sufficient ammonia has previously been converted to nitrate. Fortunately, the oxidiation of ammonia and the reduction of nitrate are not complementary processes thereby allowing nitrate to accumulate under aerobic conditions. However, with the onset of the anaerobic state (irrigation), the accumulated NO_3^- can be quickly lost in the form of gaseous end products if sufficient soluble carbon is present. The heterotrophic microorganism which can use nitrate as the terminal acceptor of hydrogen must have available carbohydrate; otherwise the entire denitrification process is markedly diminished. For this reason the addition of readily oxidizable organic residues can promote denitrification under anaerobic conditions.

A final loss pathway involves the non-enzymic conversion of nitrite to nitric oxide (Wullstein and Gilmour, 1964). These authors presented a conventional half-cell reaction as follows:

$X + NO_2^- + H^+ \longrightarrow X^{+++} + NO + H_2O$. X can be a transition - like metal such as manganese, iron or copper. If soils contain considerable quantities of reduced Fe^{++} and Mn^{++} and NO_2^- is present, the reaction could account for significant losses of fertilizer nitrogen.

In summary, it is clear that the avenues whereby urea nitrogen may be lost as a plant nutrient are diverse. Under the right conditions each one: volatilization, denitrification and the non-enzymic oxidation of NO_2^- can result in significant losses of nitrogen. On the other hand, such losses can be greatly minimized if due attention is given to the factors which mediate such reactions.

A summary of the reaction sequences is given in Figure 1.

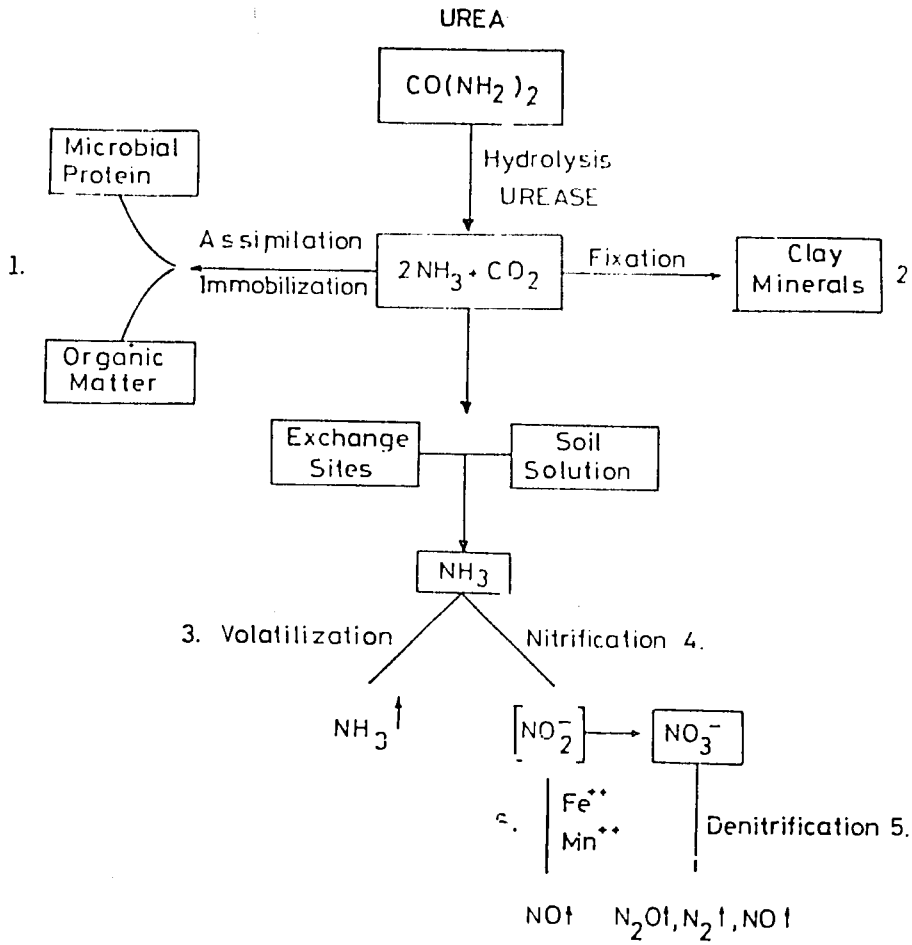

Figure 1. Pathways of nitrogen transformation in soil

TECHNICAL REPORT

Laboratory Studies

As indicated in the work plan, the laboratory studies were designed to provide data on volatilization and denitrification losses as a guide for the projected field experiments. It was expected that the results would confirm the accuracy of the methodology and thus provide a sound basis for the more expansive field trials. The objectives have been stated in the work plan on page 1 of this report.

Materials and Methods

Bulk soil was collected at both the Sids (field 6) and Gemmeiza (field 13) stations. The soil was pulverized, air dried and passed through a 10 - mesh screen. The Sids soil is non-saline and non- alkaline. The soil texture is clay loam. Cation exchange capacity is high (> 40 meq/ 100 g soil). The Gemmeiza soil is also non-saline and non-alkaline and has a clay loam texture. Cation exchange capacity is high (> 43 meq/ 100 g soil). The above information was obtained from EMCIP publication 14 (Dr. N.M. El Mowelhi and Dr. B.C. Williams)

Fisher 2 L pressure flasks were used as the soil containers. These flasks were fitted with a rubber gasket and metal spring attachement so that the glass top provided a closed system. One kg of soil was placed in the flask and distilled water added to give 50-60 % of soil WHC for the surface-applied urea treatments. Following the addition of water, urea (140 mg) was sprinkled on the soil surface. Two plastic vials, one containing 0.1 N H_2SO_4 and the other 0.1 N NaOH were placed on the soil surface and the flask closed. For the deep placement of urea 500 g of soil were placed in the flask and water added to give 50-60 % of the WHC. Then urea was sprinkled on the surface and covered with an additional 500 g of soil. The top layer of soil was also brought to 50-60 % of the WHC and the absorption vials placed on the soil. All tests were set up in triplicate and incubated at 20-22°C

The analysis for NH_3 - N as the end product of volatilization of urea was predicated on the need for a method applicable to field tests. An air flow system geared to sweep the evolved NH_3 into an appropriate absorbant

(H_2SO_4) was not considered because of the lack of electrical (pump) power at the field sites. Admittedly such a procedure would be preferred. In consequence, vials containing 0.1 N H_2SO_4 were used to absorb the evolved NH_3 in the closed pressure flask. The amount of absorbed NH_3 was determined by conventional nesslerization of the 0.1 N H_2SO_4 and reference to a previously prepared standard curve which covered a range of 0-300 μg NH_4^- N/50 ml.

A similar situation existed for the denitrification end products (NO_x). Gas chromatography would have been the method of choice. Again, however, the projected field studies dictated that we use an alternate procedure. Studies by Wullstein and Gilmour, 1964, had shown that a weak base can be used for the absorption of N_2O and NO. Therefore 0.1 N NaOH was used as the absorbant for these gases and the amount determined by colorimetry using the NO_2^- test (sulfanilamide and N-(naphtylethylenediamine). The range for the NO_2^- standard curve was 0-15 μg NO_2^- N/50 ml. In the case of N_2O and NO analysis, the intent was not to obtain a complete accounting of the denitrification end products since N_2 was not included. Instead N_2O was looked upon as an indicator gas by which information could be obtained relative to the comparative magnitude of the volatilization and denitrification processes.

Three individual phases were studied. The first study was designed to test the analysis system for NH_3 & NO_x gases and to simulate a wetting and drying soil moisture regime. Phase one was designed to demonstrate potential volatilization losses. The flasks were opened during phase two so that nitrification would take place. At the end of phase two the flasks were again closed to create anaerobic conditions for the formation of denitrification end products, NO_x gases (phase 3).

The following time schedule was used:

Start

October 19 (Flasks closed)

↓ Phase 1 - Volatilization - Denitrification

October 20 October 24 October 26

Analysis for NH_3 NO_2, NO

↓

Flasks open - Ocotber 26 - November 3

↓ Phase 2 Nitrification

Flasks closed - November 3 - November 7

↓ Phase 3 - Denitrification

Analysis for NO_x - November 7

A second study was carried out for the purpose of determining the influence of urea concentration on volatilization of ammonia. Only surface-applied urea was used at concentrations of 70, 140, 210, 280 and 350 mg urea/kg soil. Duplicate flasks were incubated at 20°C for 4 days and the samples assayed for NH_3. A similar experiment was conducted to evaluate the effect of temperature and urea concentration on ammonia volatilization. In the latter case soil temperatures were adjusted prior to incubation by the addition of water and the flasks placed in controlled temperature incubation (35 °C, 30 °C, 20 °C and 10 °C). Ammonia volatilization was determined after 7 days' incubation. These tests were set up in triplicate.

Results

The laboratory data given in Table 1 summarize volatilization losses for the Sids and Gemmeiza soils. In the 7-day test period the greatest loss was observed during the first 48 hours with far less volatilization noted during the 2-4 day and 4-7 day incubation periods. All three indices of volatilization, total µg NH_3 , µg NH_3/cm^2 and % loss depicted similar trends. Surprisingly enough, the overall percentage losses of urea-nitrogen of 0.64 for the Gemmeiza clay soil

and 0.68 for the Sids clay soil are low. However, the relatively low urea concentration (140 mg) and moderate temperature (20 °C) may have combined to give less volatilization of ammonia. Data on fertilizer placement are given in Table 2. It is clear that the procedure used (absorption of NH_3 in 1 N H_2SO_4 and nesslerization) showed the marked increase in volatilization with surface-applied urea and decrease in tests with deep applications of urea.

Table 1. Ammonia volatilization with surface-applied urea

Time (days)	Gemmeiza			Sids		
	NH_3					
	µg	µg/cm^{2+}	%loss*	µg	µg/cm^{2+}	%loss*
0 - 2	283	2.50	0.45	356	3.15	0.45
2 - 4	100	.88	0.15	66	0.58	0.10
4 - 7	26	.23	0.04	10	0.09	0.02
Total	409	3.61	0.64	432	3.82	0.68

* Based on an input NH_4- N of 63 mg

\+ Based on a soil surface area of 113 cm^2

Table 2. Influence of fertilizer placement on volatilization of ammonia.

Time (days)	Gemmeiza clay		Sids clay	
	%loss*			
	Surface	deep	Surface	deep
0 - 2	0.45	0	0.56	0.05
2 - 4	0.15	0	0.10	0.02
4 - 7	0.04	0	0.02	0.00
Total	0.64	0	0.68	0.07

* Based on urea N input of 63 mg

At this juncture in the study it became evident that temperature and urea concentration played highly significant roles in the volatilization process. Certainly earlier literature had also stressed temperature and fertilizer application rates as key mediat'ng factors.

Table 3. Influence of temperature and urea concentration on volatilization after 7 days' incubation with Cemmeiza soil.

Soil Temperature C°	µg	µg/cm²	% loss
		140 mg urea	
30	497	4.39	0.78
24	317	2.80	0.50
18	125	1.10	0.19
14	68	0.60	0.10
		350 mg urea	
30	1900	16.81	1.20
24	840	7.43	0.53
18	180	1.59	0.11
14	125	1.10	0.07

The results shown in Table 3 attest to the aformentioned observations. Only 0.1% of the input nitrogen was lost at a soil temperature of 14 °C with the 140 mg urea level and 0.07% at the higher 350 mg urea application rate. Indeed, as the temperature fell below 20 °C, volatilization loss decreased rapidly. As might be expected, greater total losses of nitrogen were observed with the higher 350 mg urea rate. Additional data on the concentration factor are given in Figure 2.

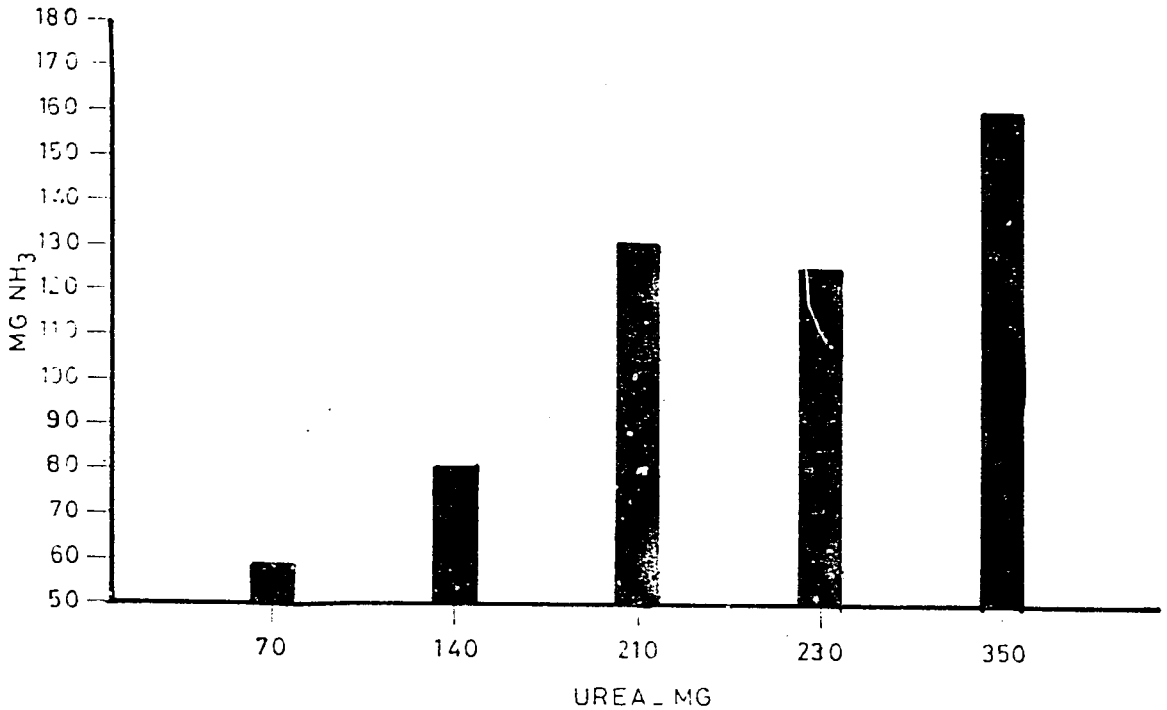

FIGURE 2 : INFLUENCE OF UREA CONCENTRATION ON VOLATILIZATION OF AMMONIUM.

Table 4. Production of NO_x as indicators of enzymic and non-enzymic reduction of nitrite and nitrate

Fertilizer Placement	Gemmeiza (13)	% loss*	Sids (6)
		- glucose	
Surface	0.0010		0.0010
Deep	0.0004		0.0007
None	0.0007		0.0006
		+ glucose	
Surface	0.0030		0.0076
Deep	0.0010		0.0017
None	0		0

* Based on urea N input of 63 mg

Denitrification trends and non-enzymic conversion of NO_3^- and NO_2^- to gaseous end products are given in Table 4. It should be understood that the data do not include N_2 and thereby present only a partial picture of the operation of these reduction pathways. In any case the data point to little loss of urea nitrogen in the form of NO_x gases. The addition of glucose increased losses 3x and 7x with the Gemmeiza and Sids soils, respectively. The lack of an available carbon source would decrease denitrification and indeed this may be the key limiting factor in such soils.

Field Studies

With completion of the laboratory tests, it was decided to design field trials. Two sites were selected, namely, Gemmeiza (field 13) and Sids (field 6). The objectives are given in the introduction to this report. These are limited to measurement of volatilization and denitrification losses and do not include other agronomic objectives.

Materials and Methods

The experimental design was split-strip block with 4 replicates. Plot area was 3.5M x 2.6M with an area of $12.6M^2$. 48 plots were used. Fertilizer rates and irrigation schedules were as follows:

Fertilizer Treatments*	Plots
1,7 - 60 kg urea-N broadcast	1, 24, 34, 39, 7, 18, 28, 44
2,8 - 30 kg urea-N broadcast	2, 23, 33, 37, 8, 17, 22, 43
3,9 - 60 kg urea-N incorporated	3, 22, 31, 42, 9, 16, 25, 48
4,10 - 30 kg urea-N incorporated	4, 21, 32, 41, 10, 15, 26, 47
5,11 - 0 nitrogen	5, 20, 35, 40, 11, 14, 29, 45
6,12 - 60 kg urea-N drilled	6, 19, 36, 38, 12, 13, 30, 46

* All plots received 15 kg P_2O_5 and 24 kg K_2O.

Irrigation of Plots - Immediately following fertilizer application - plots 1-6, 19-24, 25-30 and 43-48; 24 hours after fertilizer application - plots 7-12, 13-18, 31-36 and 37-42.

Crop - Giza 157 wheat seed planted just prior to fertilizer placement.

Gas Collection and Analysis

As in the laboratory studies, evolved gases were trapped or absorbed in 0.1 N H_2SO_4 and 0.1 N NaOH. Metal containers (Egyptian boiling pots) were used as the field jars to trap the gases evolved. These pots have a diameter of 32 cm and are 46 cm in height. After the addition of urea a brick was placed on the soil surface and plastic vials containing the absorbants were placed on the narrow edge of the brick. The open end of the metal field pot was lowered over the brick and pressed 3-4 cm into the soil. Soil was then packed around the bottom of the pot and sprinkled on the top (closed end) to minimize any potential heating effects inside the container. Field pictures are shown in figures 3 and 4.

The H_2SO_4 and NaOH field samples were transferred to glass tubes, capped and taken to the Soil Microbiology laboratory at the ARC for

Figure 3: Alignment of trap system for gaseous evolution in the field.

Figure 4: View of trap system showing containers of acid and alkaline solutions on brick before covering with baladi boiling pot.

analysis. Chemical determinations were conducted for NH_3, and NO_x gases as described for the laboratory tests. The data are expressed on a µg basis and loss indices as nitrogen lost/cm^2 and overall percentage loss. The four replicates were combined to give a mean value for eight samples. Samples were taken on day 7 and day 21.

Results

Volatilization data for the Sids clay soil are given in Table 5. Very low values were obtained for the 0-7 day interval whereas moderate ammonia evolution trends were observed for the 7-21 day period. However, in line with the laboratory results, the plots receiving surface-applied urea produced a much higher loss of nitrogen than with the other fertilizer treatments. The 60 kg drilled fertilizer plot showed only a minimal loss of nitrogen (0.12%). In all cases the loss was less than 1.0% of the input nitrogen.

Table 5. Observed volatilization of ammonia with the Sids clay soil after 21 days' incubation (Nov. 10 - Dec. 1, 1982)

Treatment Kg urea-N	µg - NH_3 days 0 - 7	7 - 21	Total µg - NH_3	µg/cm^2	% loss*
60 - surface	210	5000	5210	8.68	0.61
30 - surface	170	1600	1770	2.95	0.41
60 - incorporated	185	1900	2085	3.47	0.24
30 - incorporated	105	1400	1505	2.50	0.35
60 - drilled	80	960	1040	1.73	0.12
None	75	540	615	1.02	--

* % loss based on input of 854 mg N/600 cm^2 urea nitrogen for the 60 kg plots and 427 mg N/600 cm^2 for the 30 kg plots.

Data on the enzymic (denitrification) and non-enzymic reduction of nitrate and nitrite are shown in Table 6. Very small losses were observed in the Sids plots. As with the volatilization readings, greater nitrogen losses were found with surface-applied urea, an indication

of some oxidation of NH_4^+ to NO_2^- and NO_3^-, particularly during the 7 - 21 day incubation period. However, on a comparative basis, volatilization losses were over 100x greater than either denitrification or non-enzymic losses.

Table 6. Observed conversion of nitrate and nitrite to NO_x gases with the Sids clay soil after 21 days incubation (Nov. 10 - Dec. 1, 1982)

Treatment Kg urea-N	µg - N_2O, No days 0 - 7	7 - 21	Total µg - N_2O, NO	µg/cm^2	% loss*
60 - surface	7.5	24.7	32.2	0.05	0.0037
30 - surface	5.4	8.9	14.3	0.02	0.0032
60 - incorporated	5.8	16.8	22.6	0.04	0.0026
30 - incorporated	5.5	13.3	18.8	0.03	0.0044
60 - drilled	4.6	6.8	11.4	0.01	0.0013
None	1.2	0.3	1.5	0.002	---

* % loss based on input of 854 mg N/600 cm^2 - urea nitrogen for the 60 kg plots and 427 mg N/600 cm^2 for the 30 kg plots.

The Gemmeiza nitrogen losses via the volatilization pathway are presented in Table 7. As with the Sids data, far greater release of ammonia occurred during the 7-21 day period. Total loss of nitrogen during the 21- day test period was over 4x greater with the surface application than with the drilled fertilizer. The other fertilizer treatments also showed less volatilization than the 60 kg surface treatment. Losses expressed in term of µg/cm^2 and on a percentage basis clearly indicate that the incorporation or drilling of the fertilizer markedly decreases the volatilization of urea nitrogen. However, as was observed at the Sids site the Gemmeiza volatilization losses cannot be regarded as extensive even though the loss for the 60 kg surface application exceeded 1.0%

Table 7. Observed volatilization of ammonia with the Gemmeiza clay soil after 21 days incubation. (Nov. 16 - Dec. 7, 1982)

Treatment Kg urea-N	µg - NH_3 days 0 - 7	7 - 21	Total µg - NH_3	µg/cm^2	% loss*
60 - surface	2400	7600	10000	16.6	1.17
30 - surface	1440	2240	3600	6.0	0.84
60 - incorporated	960	4000	4960	8.2	0.58
30 - incorporated	1040	2480	3520	5.8	0.82
60 - drilled	640	1600	2240	3.7	0.26
None	320	40	360	0.6	--

* Based on a input urea nitrogen of 854 mg, for the 60 kg application and 427 mg for the 30 kg rate.

Comparative denitrification and non-enzymic data are shown in Table 8. Only low level release of NO_x gases was detected. As with the volatilization data, higher losses were found for the 60 kg surface application which indicated that nitrification had provided nitrite and nitrate. Yet, on a comparative basis, volatilization far exceeded (> 100x) denitrification and non-enzymic losses.

Irrigation timing (immediate versus 24 hours after seeding and fertilizer additions) had no significant effect on the volatilization and denitrification of the urea.

Table 8. Observed conversion of nitrate and nitrite to NO_x gases with the Gemmeiza clay soil after 21 days incubation.

Treatment Kg urea-N	µg - NH_3 days 0 - 7	7 - 21	Total µg-N_2O-NO	µg/cm^2	% loss*
60 - surface	2.8	13.4	16.2	0.027	0.0018
30 - surface	2.4	8.3	10.7	0.017	0.0025
60 - incorporated	1.6	9.5	11.1	0.018	0.0012
30 - incorporated	2.4	6.4	8.8	0.014	0.0020
60 - drilled	2.0	8.1	10.1	0.016	0.0011
None	0.5	0.3	0.8	0.001	---

* Based on an input of urea nitrogen of 854 mg for the 60 kg application and 427 mg for the 30 kg rate.

The laboratory (Table 1) and field data (Tables 5 and 7) call attention to the overall similarity of the results for surface-applied urea. If fertilizer concentration and temperature are ignored, essentially identical percentage losses were obtained (laboratory - 0.68% and field - 0.6%) in the Sids clay soil. However, the Gemmeiza field tests showed higher volatilization losses (1.17%) than were observed in the laboratory (0.64%). In general, both the laboratory and the field studies provided evidence that only minimal volatilization had occurred.

Discussion

A primary objective of the study was to develop a procedure whereby volatilization and denitrification losses could be measured and evaluated under field conditions. The laboratory experiments provided the necessary procedural information. One important constraint was the lack of an electrical power source at both the Gemmeiza and Sids sites which prevented the use of an air flushing system. In consequence, the absorption technique was adopted with the realization that complete

capture of evolved gases might not occur. It was hoped, however, that the absorption technique would provide comparative data. The results of the laboratory and field tests supported this contention. The observed differences in volatilization between surface, incorporated and drilled fertilizer amply attested to the validity of the absorption method. Thus, valid treatment comparisons were possible.

Early literature (Hamissa and Shawarbi, 1962) demonstrated that greater volatilization losses occur with surface-applied urea. Our study supports this observation, particularly in the case of the field data. Thus, the current recommendation that urea should be either incorporated or drilled into calcareous soils is indeed valid. This point takes on added significance when calculations are made involving total feddans planted to wheat and the net loss in fertilizer investment. A loss of 1.17% of urea nitrogen with surface-applied urea (60 kg) at Gemmeiza would mean approximately 1 kg lost per feddan. With a total of 1.4 million feddans in Egypt planted to wheat and the cost of urea L.E. 6.40/50 kg, nearly L.E. 400,000 are lost per season by surface volatilization.

Other questions arising from the current study require consideration. Although the volatilization losses rarely exceeded 1.0% in our study, other published papers have reported losses ranging as high as 10-20% of applied urea nitrogen. Such losses should be defined in turns of the conditions under which they occurred. For example, high soil temperatures (30°-40°C) undoubtedly increase volatilization rates. In addition, as the calcium carbonate content of a soil rises so does the volatilization process. These and other chemical and physical factors must be considered when attempting to predict the overall percentage loss of nitrogen. In the present study, the soil temperatures at the Gemmeiza and Sids stations ranged from 12 ^{o}C to 16 ^{o}C. Such low temperatures would tend to decrease both the rate and the magnitude of the volatilization of urea. The observed lag (0-7 days) in the release of NH_3, NO_x gases followed by a marked increase in the 7-21 day period may also reflect the low soil temperatures at both test sites. It is not surprising, therefore, that relatively low volatilization of urea nitrogen was found with both the Gemmeiza and Sids clay soils. Nevertheless, the volatilization problem cannot be ignored

during the Egyptian winter crop season but can be minimized by incorporation of the urea.

A large number of microbial species can reduce nitrate to nitrite (nitrate reducers) and selected species have the enzymes requisite for the complete reduction of nitrate to gaseous end products (denitrifiers). Under the right conditions these biological reductive pathways (Figure 1) can result in extreme nitrogen losses. Two key soil states must exist. Since nitrate is being used as the terminal acceptor of hydrogen during the oxidation of soluble carbon, it is imperative that sufficient carbon be present. Otherwise little or no microbial utilization of nitrate as a terminal hydrogen acceptor will occur and thereby far less nitrogen will be lost as dimers of N gases (NO_x). It is for this reason that the addition of glucose (Table 4) increased the loss of nitrogen in both the Sids and Gemmeiza clay soils. A second constraint when using urea as the fertilizer is that the oxidation (nitrification) of NH_4^+ to NO_2^- and NO_3^- must supply adequate quantities of the terminal acceptor to meet the respiration demands of the denitrifiers. The observed increase in the release of NO_x gases (Tables 6 and 8) during the 7-21 day period undoubtedly reflects the buildup of nitrate or nitrite in the test system. However, low temperatures and a low partial pressure of O_2 will inhibit the nitrification process. On the other hand, anaerobic conditions favor the utilization of nitrate as a terminal acceptor of hydrogen. When all these factors are considered, it is not surprising that little evidence of extensive biological conversion of nitrate to gaseous end products was found. Admittedly, N_2 was not determined and furthermore the use of NO_x gases as indicator gases cannot establish the denitrification potential of the test soils. Yet, if all these factors are considered, namely, low levels of soluble carbon, low temperatures, moderate O_2 tension and insufficient nitrate, we are led to the conclusion that at least during the winter period, denitrification is not a major loss pathway.

The non-enzymic reduction of nitrite to nitric oxide could not be accurately evaluated. However, preliminary laboratory experiments involving the addition of NO_2^- and reduced iron to the Gemmeiza clay soil indicated that nitric oxide was formed. The relatively high iron and manganese content of the test soils provides at least one reaction

component and, if nitrite appears, the reaction may proceed. Certainly low level and often non-detectable quantities of evolved nitric oxides could, over long periods of time, constitute an important loss pathway, particularly in soils with high transition metal contents.

A final point for discussion relates to the physical and chemical nature of the Gemmeiza and Sids clay soils. With soil incorporated urea, the high clay content of both soils provides maximum exchange sites for holding the NH_4^+ cation on the base exchange complex. In addition, the montmorillonite clay and related expanding clay lattice give ample opportunity for fixation of the NH_4^+ cation. Because of the relatively low calcium carbonate level (1-2%) these soils cannot be characterized as calcareous. The immobilization of ammonium nitrogen in both the organic matter fraction of soils and in the form of microbial protein also reduces the potential for volatilization. All such factors should be considered in the evaluation of volatilization and denitrification losses.

Summary

1. A laboratory and field procedure was developed to evaluate volatilization and denitrification pathways of nitrogen loss with urea as the source of nitrogen.

2. With the Gemmeiza and Sids clay soils, volatilization losses rarely exceeded 1% of the input urea nitrogen. This rather low volatilization value is explained primarily on the basis of low soil temperatures characteristic of the Egyptian winter period.

3. Surface-applied urea showed far greater volatilization losses than were found for drilled or incorporated urea. On a fertilizer management basis, surface application of urea should be avoided.

4. Under the conditions of this study, non enzymic and enzymic denitrification did not constitute a major loss pathway since losses rarely exceeded 0.002% of the input urea nitrogen. These very low values are explained promarily on the basis of the low soil temperatures and the lack of nitrate and oxidizable carbon.

5. Non-enzymic losses relating to the oxidation of Fe^{++} to Fe^{+++} and concomitant reduction of NO_2^- to NO were not resolved but deserve further study.

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