Effect of Sulfuric Acid on Ammonia Volatilization under Furrow Irrigation¹

T. A. YAHIA AND J. L. STROEHLEIN2

ABSTRACT

In this study, anhydrous ammonia (NH₃) was applied in the irrigation water along with and without the additional sulfuric acid (H₂SO₄). Ammonia losses by volatilization were measured indirectly by measuring nitrogen (N) in soils, plant tissue and irrigation water at two field locations. This study showed that adding H₂SO₄ with irrigation water reduces the loss of nitrogen ammonia volatilization, especially when the irrigation water contained high levels of sodium relative to calcium. The reduction was as high as 49%.

According to this study H₂SO₄ application is recommended as the best and most economical way to minimize or prevent NH₃ volatilization losses under alkaline soil conditions, especially for those waters high in Na. In particular, if summer application is necessary, the acid rates should be sufficient to reduce the water pH to near neutral during NH₃ application. The data indicated that losses took place mostly from the soil and increased with distance along irrigation furrows.

INTRODUCTION

Anhydrous ammonia is becoming the most common source of fertilizer nitrogen because of its high analysis (82% N), convenience of handling, and lower cost than other commonly used materials. Ammonia may be injected into the soil at any time prior to or during the growing season. After the crop is established, however, NH₃ is often added to the irrigation water. Ammonia applied to the water is a very simple and inexpensive method of application and can be done without driving equipment through the field. In addition the desired amount of NH₃ can be metered into the water very precisely.

Loss of NH₃ by volatilization is of concern to soil scientists and farmers. Mills *et al.* (3) concluded that NH₃ losses by volatilization increase as pH increases, as a result of the increase of OH activity. Total N loss, however, was reduced by the presence of plants as compared with bare-soil treatments. Volatilization of NH₃ presumably occurred as a consequence of the hydrolysis of applied urea to (NH₄)₂CO₃ which could raise the pH of the surface layer of the soil. Volk (6) reported that increasing soil pH decreased the NH₃ adsorption potential of Florida soils, and resulted in greater volatilization from applied urea.

¹Contribution from the Department of Soils, Water and Engineering, The Univ. of Arizona. Supported in part from a grant by the Arizona Mining Assoc. and a scholarship to the senior author from the Univ. of Al-Fateh at Tripoli, the S.P.L.A.J.

²Graduate student and Associate Professor, respectively. The senior author is now a staff member of the Soil and Water Department of Univ. of Al-Fateh at Tripoli, the S.P.L.A.J.

Sulfuric acid application in the irrigation water was found to lower the pH of both the water and the soils, and was found to reduce the concentration of NH₄OH relative to total N applied as NH₃ principally, by lowering pH. Thus simultaneous application of acid and ammonia helps to control ammonia loss, Miyamoto et al. (4).

The objectives of this study were (1) to indirectly measure N losses from ammoniated and acidified water by soil, water and tissue analysis; (2) to determine the distribution and forms of N from treated waters in the irrigation ditch and down the furrow, and (3) compare the results of yield of cotton (Gossypium hirsutum L.) between the treated and the untreated plots under the two different soil and water conditions.

MATERIALS AND METHODS

Two field experiments on cotton were conducted at two different locations for the purpose of comparing the results under two different soil and water conditions. The properties of soils and waters of the two locations are listed in Tables 1 and 2 respectively.

Anhydrous ammonia (NH₃) versus NH₃ plus H₂SO₄ applied in the irrigation water was applied. The rates of fertilizer and H₂SO₄ application are shown in the general

information table of the appendix A.

Soil samples of about 10 cores per plot 15 cm deep from the side of the beds were collected periodically. Sampling the soil in this manner has been found to give the best estimate of available nitrogen in irrigated soils (5) because it takes into account the salt movement from furrow to bed under furrow irrigation. The collected soil samples before and after treatment were air dried and sieved through a 6.23 mm screen and analyzed (routine analysis). Petioles from the youngest mature leaf were taken several times during the season from 25–30 plants per plot. These sampling periods correspond roughly to the time of the early stage of growth, first flower, first boll, first open boll and just prior to harvesting. The petiole samples were analyzed for NO₃–N. Water samples were also taken at 200 m intervals along the ditch starting from the well and then through the field and analyzed for NH₄–N, NO₃–N by Kjedahl method, pH and, other important ions using the atomic absorption technique.

Table 1. Properties of experimental soils collected from the two study areas.

		Saturation extract							
	pН	$EC_e \times 10^3$ mmhos/cm	TSS ^a ppm	Na me	K eq/l	ESP %	NO ₃ -N	P	CEC meq/100 g
Marana Farm									
Pima clay loam	8.0	0.4	273	2.7	0.3	5.0	12.7	2.3	31.5
Buckelew Farm									
Gila loam	7.8	0.7	490	4.2	0.3	9.0	11.5	2.4	32.5
Vinton fine sandy loam	7.8	0.6	420	3.7	0.2	7.0	11.5	2.6	20.6

[&]quot;Total soluble salts.

Table 2. Chemical properties of water wells used for the study.

Water	$EC \times 10^3$						mg/l	or ppm	l.			
sample		pН	TSS	Ca	Mg	Na	Cl	SO ₄	HCO ₃	CO ₃	F	NO ₃ -N
Marana	0.35	7.5	383	100	4.0	36	26	48	166	0	0.2	2.7
Buckelew	0.41	7.9	388	17	1.0	71	51	72	166	0	1.6	8.9

The cotton cultivars used in these experiments, the planting dates, harvesting dates, fertilizer application rates and H₂SO₄ rates, are shown in the general information table in the appendix A.

Standard cultural practices for the area including cultivating, irrigating and pest control, were used at both locations. Cotton was harvested by a mechanical picker. Two rounds were made in each treatment area at one site. In the other site one round was harvested. In both cases yields are presented in terms of seed cotton in pounds per acre.

A multivariate analysis of variance was run for all the cotton data collected at different dates. Three main variable factors were considered (Treatment, Blocks and Pairs). A separate multivariate analysis was then run for the combined dates that showed significant difference. Furthermore, the Least Significant Differences Test (LSD) was used to detect where the differences are. A Linear Contrast Test was also run to show whether or not the soil plant nitrate-nitrogen varied linearly down the field.

RESULTS AND DISCUSSION

Soil analysis

The results of analysis of soils presented in Table 3 show that soil NO₃-N content increase for a time following N application, compared with the initial contents, gradually declined, then started increasing again toward the end of the season. The increase could have been a result of a decreased rate of cotton growth following the last irrigation on August 31 and defoliation prior to harvesting. Nitrification could have continued since the soil was warm and not completely dry. The increase in NO₃-N of the acid treated plots could be evidence of reduced NH₃ volatilization. With the exception of the first two months (May and June) in all cases, the NO₃-N content of soil samples was higher in the acid treated plots compared with the control; the difference between the treatment and the control was statistically significant at the 5% level. The same pattern took place for NH₄-N as seen in Table 4.

Data presented in Fig. 1 show a linear decrease of NO₃-N of the soils down the field. This leads to the conclusion that the length of irrigation runs should be shortened if anhydrous ammonia is to be applied in the irrigation water. This could be of particular concern on light-textured soils, as sandy soils lack the capacity for adsorption of large quantities of ammonia and excessive losses will take place (2).

Table 3. Nitrate-N (NO₃-N) in the soils during the season (Buckelew Farm, 1976) in ppm.

	May	June	July	August	September	October
Control	13.7	8.0	12.7	6.0	6.5	11.0
Treatment	13.0	7.8	13.2	7.5	9.7	16.2

Table 4. Total-N $(NH_4-N + NO_3-N)$ in the soils during the season (Buckelew Farm, 1976) in ppm.

	May	June	July	August	September	October
Control	20.5	16.5	_	9.7	11.8	15.1
Treatment	19.5	15.8	-	11.5	16.6	19.9

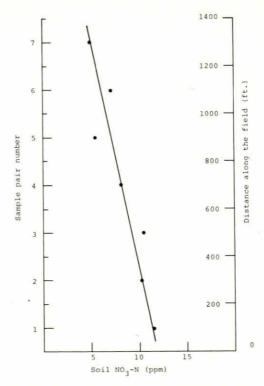


Fig. 1. Variation of soil nitrogen (NO₃-N) along the field beginning at the irrigation ditch (Buckelew Farm).

The data presented in Table 5 show the decrease of NO₃-N as the growing season progressed. This pattern was to be expected; however, the levels at Marana were slightly in excess while those at Buckelew's could be considered to be minimal for good yields (5); this is very clearly indicated by the shape of the Figs. 2 and 3. Acid treatment apparently reduced the NH₃ loss as indicated by the higher levels of NO₃-N in plants which received acid-treated water. The difference between acid treatment and control was highest in July (approximately 4000 ppm in Buckelew Farm) during the hottest part of the season. The low petiole NO₃-N levels in August and September are normal and are due to the high N consumption by the plant during this period of heavy fruiting.

Table 5. Nitrate-N in the cotton petioles during the season in ppm.

	June	July	August	September
a. Buckelew I	Farm			
Control	6,489	5,153	1,048	559
Treatment	6,554	5,842	1,464	814
b. Marana F	arm			
Control	22,600	13,100	5,832	4,256
Treatment	23,400	17,000	6,022	5,645

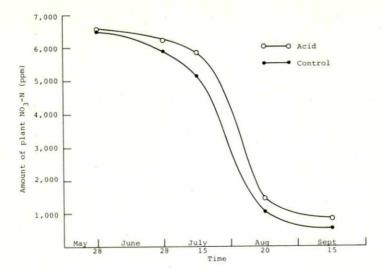


Fig. 2. Effect of H₂SO₄ on plant nitrogen (NO₃-N) and its variation during the season (Marana Farm).

Data presented in Table 6 show the increase of pH as a result of NH_3 application. The maximum pH reached is 9.6. Under field conditions, however, and as a result of CO_2 pressure, the reaction is less alkaline than was expected. The acid treatments reduced the carbonate and bicarbonate concentration and lowered the pH levels of the irrigation water. The data also showed that acid treatment increased the NO_3 -N content of the irrigation water as compared by the control, but decreased the NH_4 -N, however, the total $N(NH_4$ -N + NO_3 -N) appeared to increase very slightly with the exception of the first sample which is allocated at the beginning of the furrow near the ditch where not much variation is expected.

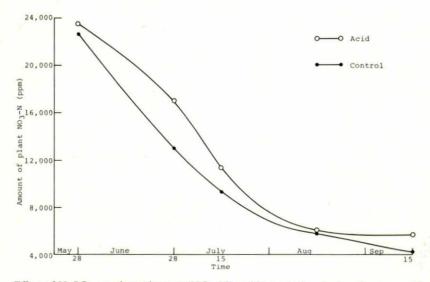


Fig. 3. Effect of H₂SO₄ on plant nitrogen (NO₃-N) and its variation during the season (Buckelew Farm).

Table 6. Representative water analysis from Buckelew Farm (samples collected July 3-7, 1976).

				mg/l or ppm									
Sample Number	pН	$\frac{EC\times 10^3}{mmhos/cm}$	TSS ^a ppm	Ca	Mg	Na	Cl	SO ₄	HCO ₃	CO ₃	F		NH ₄ -N
16	7.9	0.5	369	9	0.4	78	18	126	107	0	1.2	1.6	7.9
2	9.6	0.3	282	21	0.1	79	17	9	117	41	1.4	0.3	10.3
3	7.7	0.5	345	10	0.9	75	16	126	103	0	1.6	1.8	7.0
4	9.6	0.3	289	21	0.3	75	17	9	127	38	1.2	0.4	8.3
5	7.6	0.5	346	6	0.4	76	16	132	103	1.2	1.6	1.8	7.6
6	9.5	0.3	322	39	0.2	77	17	9	142	36	1.2	0.4	8.3
7	7.6	0.5	349	8	0.6	77	16	132	105	0	1.4	1.8	6.8
8	9.4	0.3	276	20	0.1	77	17	9	137	36	1.3	0.5	7.5
8	7.5	0.5	356	7	0.5	78	16	132	112	0	1.6	1.8	6.8
10	9.5	0.3	306	21	0.1	78	18	9	142	36	1.2	0.4	7.7
11	7.3	0.5	348	9	0.5	74	16	132	107	0	1.6	1.8	6.3
12	9.4	0.3	292	21	0.1	75	17	9	127	41	1.5	0.4	7.5

[&]quot;Total soluble salts.

^bNumbers refer to sample sites in Fig. B.2, Appendix B.

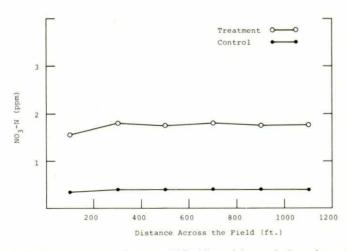


Fig. 4. Effect of H₂SO₄ on water nitrogen (NO₃-N) and its variation along the cotton field (Buckelew Farm, July, 1976).

Table 7. Effect of H2SO4 on cotton yields.

Plot	Marana Farm							
	1ª	2"	3	44	5			
•	1160	1130	1040	990	1060			
		Bu	ckelew Fa	rm				
	Rep ¹	Rep ²	Rep ³	Total	Average			
Treatment	1215	1250	1350	3815	1257			
No treatment	1130	1110	1135	3375	1125			

[&]quot;Acid treated plots as shown in Fig. 1B, Appendix B.

Table 8. Effect of treatment as shown by the multi-variate analysis of variance data at both locations.

			100.40	1255	TSS	Soil NO ₃ -N	Plant NO ₃ -N
Treatment	ESP %	pH	Na K meq/l		ppm		
a. Buckelew Farm							
Control	_	7.952**	5.603*	0.3031	600.4**	7.898*	3725*
Treatment	_	7.870**	6.034*	0.3266	679.2**	9.262*	4015*
b. Marana Farm							
Control	2.063	_	-	-	640.9	18.93	5114
Treatment	1.667	Apple	-	_	711.9	19.71	5364

^{*}Significant (5% level).

Data shown in Fig. 4 show no difference in the NO₃-N distribution along the field neither in the control nor in the treated plots, as an indication of the uniformity of distribution of NH₃ in the irrigation water.

The data presented in Table 7 indicate that acid treatment can have a significant effect on yield of cotton if higher rates of acid were used. The rates used were not high enough to totally reduce the amount loss of NH₃ during the hot season especially at Marana Farm.

Statistical analysis:

The results of the multivariate analysis of variance presented in Table 8 showed a significant effect of acid treatment on the soil pH, Na, TSS, soil NO₃-N and plant NO₃-N at Buckelew Farm. No significant effect was found at Marana, which was expected because there was no soil or water problem and the available soil N level was adequate. The analysis also indicated some statistical significant difference at the various sampling dates. The significant difference was at the 1% level for the TSS, soil NO₃-N, plant NO₃-N and ESP at Marana but at the Buckelew Farm the difference was significant only for TSS and ESP and it was also at the 1% level.

Table 9. Variation of soil properties, soil NO₃-N and plant NO₃-N due to sampling dates as shown by the Least Significant Differences Test.

	ESP —	TSS	Soil NO ₃ -N	Plant NO ₃ -N			
Dates	%	ppm					
a. Buckeley	v Farm**						
2	_	615.2ª	7.650a,c	6046"			
3	_	953.1 ^b	12.980^{b}	5498h			
4		501.6°	7.400^{a}	5721°			
5	-	603.9a	6.715d	1256d			
7		519.1°	8.116°	702.9e			
LSD 0.05	_	22.41	0.49	84.73			
b. Marana	Farm						
3	1.563"	865.4ª	19.76a	5891°			
4	1.550^{a}	714.7b	23.69^{b}	5573 ^b			
5	2.500^{b}	472.8°	14.45°	4334°			
LSD 0.05	0.14	38.75	2.01	86.38			

^{**}ppm concentrations are significant at the 5% level.

^{**}Highly significant (1% level).

A Least Significant Difference Test was run to detect where the difference exists. The data presented in Table 9 showed variation between sampling dates for almost all the tested values which are indicated by the different letters. The same letters, however, indicate that the values are statistically equal. This leads to the conclusion that sampling date is a very important consideration, especially when dealing with soil properties such as TSS and soil N.

LITERATURE CITED

- Chapman, H. D., G. F. Lieberg and D. S. Rayner. 1949. A Lysimeter investigation
 of nitrogen gains and losses under various systems of cover-cropping and fertilization, and a discussion of error sources. Hilgardia 19: 57–128.
- 2. McDowell, L. L. and G. E. Smith. 1958. The retention and reaction of anhydrous ammonia on different soil types. Soil Sci. Soc. Am. Proc. 22: 38–42.
- 3. Mills, H. A., A. V. Barker and D. N. Maynard. 1974. Ammonia volatilization from soils. Agron. J. 66: 355–357.
- Miyamoto, S., J. Ryan and J. L. Stroehlein. 1975. Sulfuric acid for the treatment of ammoniated irrigation water. I. Reducing ammonia volatilization. Soil Sci. Soc. Am. Proc. 39: 544–548.
- Ray, H. E., T. C. Tucker and L. R. Amburgey. 1964. Soil and petiole analysis can pinpoint cotton's nitrogen needs. Arizona Agr. Exp. Sta. Folder 97.
- 6. Volk, G. M. 1961. Gaseous loss of ammonia from surface applied nitrogenous fertilizers. J. Agr. Food Chem. 9: 280–283.

APPENDIX A

GENERAL INFORMATION TABLE

Variato	Buckelew Farm	Marana Farm Stoneville 213
Variety	Deltapine 16	Stoneville 213
Planting date	Apr. 10, 1976	Apr. 9, 1976
Harvesting date	Oct. 7, 1976	Nov. 2, 1976

Fertilizer application rates

	Lbs of NH	Acre
Pre-irrigation	33.6	30 lbs N/Acre
1st irrigation	28.4	0
2nd irrigation	32.4	54 lbs NH ₃ /Acre
3rd irrigation	14.6	54 lbs NH ₃ /Acre
4th irrigation	0	0
	H_2SO_4 R	ates
Pre-irrigation	63	0
1st irrigation	63	0
2nd irrigation	63	79
3rd irrigation	63	79
4th irrigation	0	0

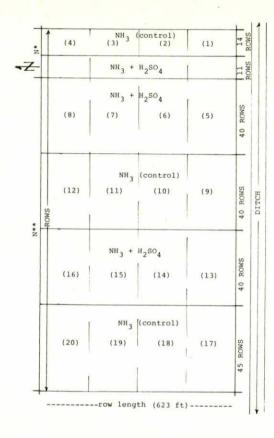


Fig. B.1. A sketch of the field showing the locations of sampling sites at the Marana Farm. N* = no nitrogen fertilizer was applied at preplanting time. N** = nitrogen fertilizer was applied at preplanting time.

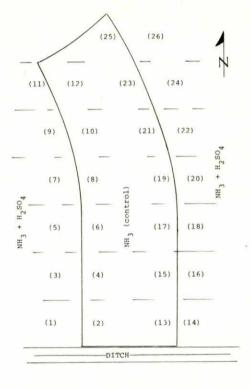


Fig. B.2. A sketch of the field showing the locations of sampling sites at the Buckelew Farm.

تأثیر حام<mark>ض الکبریتی</mark>ك علی تطایـر ا**لامونیا تحـت** الری فـی خطـــــوط * ——————

د الطاهر أدمد يحيى د م ج ل سترولايــــن

المستخلص

فى هذه الدراسة اضيفت الامونيا اللامائية فى مياه الرى مع وبدون حامض الكبريتيك وتم قياس الامونيا المتطايرة وذلك بقياس النيتروجين فى التربة والنبات وكذلك مياه الرى وتم ذلك فى حقلين من القطن •

من هذا البحث يتضح أن اضافة حامض الكبريتيك مع مياه الرى يقلل الفاقد من النيتروجين على هيئة امونيا وخاصة فى مياه الرى المحتــواه على نسب عالية من الصوديوم مقارنة بالكالسيوم ، وقد تصل نسبـــــة التخفيض فى الفاقد الى ٤٩ ٪ ،

طبقا لهذه الدراسة ومن الناحية الاقتصادية فانه ينصح باضافـــة حامض الكبريتيك للحد أو منع تطاير الامونيا تحت ظروف التربة القلوية ، وخاصة عند استعمال مياه الرى ذات النسب العالية من الصوديوم، وبالذات فى فترات الصيف حيث أن تركيزات الحامض يجب أن تكون كافية لتخفيــــف درجة الحموضة الى درجة التعادل أثناء اضافة الامونيا ،

وقد اتضح من النتائج أن معظم الفقد قد حدث فى التربــــة وزاد معدل الفقد مع امتداد خطوط الرى ·