# EFFECT OF TEMPERATURE AND WATER QUALITY ON NITROGEN LOSS FROM ARIZONA IRRIGATION WATERS E. Randall Norton The University of Arizona Safford, AZ Jeffrey C. Silvertooth The University of Arizona Tucson, AZ

#### Abstract

A laboratory study was initiated to investigate the potential loss of fertilizer nitrogen (N) through volatilization at four different temperatures (25, 30, 35, and 40°C) out of irrigation waters collected from a number of Arizona locations. Complete water analysis was conducted on each of the water samples. A 300 ml volume of each water was placed in 450 ml beakers open to the atmosphere in a constant temperature water bath with 10 mg of analytical grade  $(NH_4)_2SO_4$  added to each sample. Small aliquots were drawn at specific time intervals over a 24 hour period and then analyzed for  $NH_4^+$ -N concentrations. Results showed potential losses from volatilization to be highly temperature dependent. Total losses (after 24 hours) ranged from 30-48% at 25°C to over 90% at 40°C. In this study where  $(NH_4)_2SO_4$  was used as the N source, the initial concentration of  $SO_4^-S$  in the solution had a repressive effect on volatilization due to the decreased availability of free  $NH_4^+$  in waters with high initial  $SO_4^-S$  concentrations due to the formation of complex ion pairs  $(NH_4SO_4^-)$ . It was also observed that at lower temperatures complexation and ion pair formation affected volatilization of  $NH_3$  by reducing the  $NH_4^+$  activity in solution and thereby reducing  $NH_3$  volatilization. Potential volatilization loss of fertilizer N from these irrigation waters was found to be significant and should be considered when making decisions regarding fertilizer N applications for crop production in Arizona.

#### **Introduction**

Total N in the soil has been reported to occur at levels as high as 4,000 kg ha<sup>-1</sup> to a depth of 40 cm (Stevenson, 1982), but very little of the total N contained in the soil is available for plant uptake and utilization. Due to the lack of available N native to the system, N in the form of manufactured fertilizers is commonly applied in crop production systems to produce optimum yields. Fertilizer N is a comparatively inexpensive input in irrigated crop production systems and to ensure adequate amounts are available to avoid deficiency, excess amounts are commonly applied. This can lead to low fertilizer N efficiencies, increased costs, and increased potentials for ground and surface water pollution.

Efficient management of N in a soil plant system is often difficult due to the various transformations to which N is subjected. Transformations that lead to a loss of available N include the conversion of inorganic (available) N to organic (unavailable) N through immobilization and the conversion of  $NO_3$ -N to  $N_2O$  and  $N_2$  through denitrification, losses through  $NO_3$ -N leaching, and losses due ammonia volatilization all contribute to a decline in efficiency of fertilizer N (Jansson and Persson, 1982). In order to increase the efficiency with which fertilizer N is applied and utilized by plants it is critical that an attempt be made to quantify and characterize the potential fates of fertilizer N.

Loss of fertilizer N has been estimated to range from 20% to 80% of applied N (Catchpoole and Henzel, 1975; Henzel, 1972; Lemon, 1978; Hargrove et al., 1977; Hargrove and Kissel, 1979; and Power, 1980). One potential loss that has become increasingly critical with the increase in the use of urea over the past 20 years is ammonia volatilization. It has been shown that several factors influence the loss of fertilizer N through ammonia volatilization.

Sherlock and Goh (1985) described N volatilization from urea to be a function of several factors including: (i) hydrolysis rate, which is temperature dependent; (ii)  $NH_3$  exchange between the soil and the atmosphere; (iii) exchange between  $NH_4$  in soil solution and exchange sites in the soil; and (iv) equilibrium conditions given by the following reaction:

Application of N fertilizers through irrigation water has become increasingly popular. This method allows the producer to apply fertilizer with minimal costs associated with the application. However, in open irrigation systems such as furrow and sprinkler irrigation there is a potential for  $NH_3$  volatilization from the water prior to entering the soil (Miyamoto et al., 1975; Henderson, 1955). This is especially true for  $NH_4^+$  based fertilizers and any other form containing free  $NH_3$  such as anhydrous  $NH_3$ . This problem can be exacerbated by high pH waters (Miyamoto et al., 1975). Henderson (1955) found that loss of fertilizer N applied through sprinkler jets was most directly correlated to the pH of the fertilizer solution and that by controlling the pH of the fertilizer solution mixed with the irrigation water subsequent losses due to volatilization were mini-

mized. Volatilization losses were as high as 70% of applied N as the pH of the fertilizer solution approached 10 and reduced to less than 10% when pH was maintained at 8 or less (Henderson, 1955).

DuPlessis and Kroontje (1964) showed that an increase in  $OH^2$  concentration of a soil solution would favor a shift to  $NH_3$  in the reaction:

$$NH_{4}^{+} + OH^{-} \Leftrightarrow NH_{4}OH \Leftrightarrow NH_{3}^{+} + H_{2}O$$
 eqn. 2.

An increase in solution pH will lead to an increase in the concentration of  $NH_3$  and thus an increase in the potential for  $NH_3$  volatilization. For example, at pH 6.0, 7.0, and 8.0 the mole fraction of  $NH_3$  in equilibrium with  $NH_4OH$  and  $NH_4^+$  is 0.026, 0.26, and 2.6 respectively (Ferguson, 1984).

Miyamoto et al. (1975) reported N losses of up to 73% from irrigation waters. The addition of  $NH_3$  or  $NH_4^+$  based fertilizers to irrigation water results in the formation of various forms of N including:  $NH_{3(aq)}$ ,  $NH_4OH$ ,  $NH_4^+$  and other ion pairs depending upon the ionic composition of the water. A partial pressure gradient of  $NH_3$  will develop between the irrigation water and the atmosphere. The dissolved ammonia once exposed to the atmosphere is then readily subject to volatilization (Miyamoto, 1975). DuPlessis and Kroontje (1964) proposed the following set of reactions (eqn. 3 and 4) to describe the addition of ammonium sulfate to an aqueous solution.

$$(NH_{4})_{2}SO_{4} \Leftrightarrow 2NH_{4}^{+} + SO_{4}^{2}$$
 eqn. 3

$$NH_4^+ + OH \Leftrightarrow NH_3 + H_2O$$
 eqn. 4.

The state of these equilibrium reactions will be dependent upon several factors including temperature and ionic composition of the water (common ion effect, salt effect, complexation). Depending on the ionic composition of the solution, other reactions will take place affecting the activity of NH<sub>3</sub> and thus affecting potential volatilization.

There has been extensive research quantifying  $NH_3$  volatilization losses from soils and cropping systems. However, little research has been conducted on N loss from irrigation waters through volatilization. The objective of this study was to investigate the loss of fertilizer N through volatilization from irrigation waters from 10 different sources in Arizona. The effect of temperature on the rate of N loss was also addressed.

#### **Materials and Methods**

Ten irrigation waters were collected from various locations in Arizona. Complete water analyses were performed for each of the ten water samples prior to beginning the laboratory study. Analytical grade ammonium sulfate (10 mg) was added to 300 mL of each of the ten water samples in open 450 mL beakers. Beakers were then placed in a shaking water bath to maintain constant temperature. Small aliquots (10 ml) were drawn starting at time 0 (time of beaker placement into the water bath) and at 0.25, 0.5, 1, 2, 4, 6, 8, 12, and 24 hours. Each water sample was replicated four times at each of four temperatures ( $25^{\circ}$ C,  $30^{\circ}$ C,  $35^{\circ}$ C, and  $40^{\circ}$ C) for a total of 1,600 experimental observations. Aliquots were then analyzed for NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N using an Alpkem continuous flow analyzer (Alpkem Corporation, Perstorp Analytical, 151 Graham Road, P.O. Box 9010, College Station, TX 77842).

Data was subjected to analysis of variance with temperature as the main effect and water source as the subunit effect. Data was also subjected to muti-variate linear regression analysis to determine which water quality characteristic most highly correlated with loss of N from the irrigation water sample. Linear regression was also performed to examine the rate of N loss as a function of time. All statistical analyses were performed according to guidelines outlined by Gomez and Gomez (1984) and the SAS intitute (1994).

#### **Results and Discussion**

The ten Arizona locations associated with each water source are shown in Table 1. Locations were selected that sampled a variety of agricultural waters used for irrigation in locations that ranged from 32 meters to just under 1000 meters in elevation. A complete characterization of each of the ten water sources was performed. Results from these analyses are shown in Table 2.

## Analysis of Variance

Total percent N loss was calculated for each of the ten water sources at each temperature by subtracting the final concentration (time = 24 hours) from the initial concentration (time = 0 hours) and dividing by the initial concentration of  $NH_4^+$ -N. Results of the overall analysis of variance demonstrated a significant difference due to the water source and a significant difference due to the wate

ence due to temperature with observed significance levels (OSL) <0.0001 for both effects. A significant interaction between water source and temperature was also observed (OSL = 0.0394). To investigate the significant interaction term, percent loss was plotted as a function of temperature for each of the ten irrigation sources (Figure 1). Regression of these values was also performed and the slopes of the regression equations are presented in Table 3. In general, percent loss of N from the water sources with lower concentrations of soluble salts, specifically SO<sub>4</sub><sup>-</sup>-S, increased as temperature increased, as evidenced by the larger slope value of the regression (Table 3).

Means separation tests were performed using a Student Newman Keuls (SNK) comparison of temperature by each source (Table 4). For all water sources, a significant increase in the percent N loss was observed as temperature increased. These differences were significant ( $\alpha = 0.05$ ) for each source (Table 4). Means separations (SNK) were also performed comparing water source by each temperature (Table 5). Significant differences were observed among water sources at each temperature with higher losses of N occurring in water sources with lower total dissolved salts, specifically SO<sub>4</sub>-S.

# **Regression Analysis**

Linear regression analysis was performed examining the fractional loss of  $NH_4^+$ -N as a function of time (Table 6). Fractional loss was calculated by subtracting the the concentration at time a given time (t=t) from the initial concentration (t=0) and dividing by the initial concentration. A first order model was successfully used to fit most data. However, in a few cases a second order polynomial provided the best fit. In all cases regression parameter estimates were significant at  $\alpha = 0.01$ . In general the fit of the model increased dramatically with an increase in temperature as evidenced by r<sup>2</sup> values (Table 6). Figures 2-4 show the regression curves associated with each source and temperature.

The rate of  $NH_4^+$ -N loss increases dramatically with temperature as does the general fit of the regression model. At lower temperatures a higher fractional loss of  $NH_4^+$ -N is observed early in the 24 hour period (0-5 hours). The method of analysis for  $NH_4^+$ -N measures the activity of  $NH_4^+$  in solution and does not measure total soluble  $NH_4^+$  concentration including the fraction that has been involved in ion pair formation and complexation reactions in the solution. In general, complexation in a natural water proceeds rather quickly to some state of equilibrium (Stumm and Morgan, 1996). The reactions associated with complexation and ion pair formation will also be temperature dependent. As temperature increases the energy in the solution increases which disrupts the complexation and ion pair associations. Thus, an increase in complexation or ion pair formation at the lower temperature regimes would account for the observed apparent increase in the fractional loss of  $NH_4^+$ -N at the early sample times compared to the higher temperatures.

In order to validate this theory a series of speciation simulations were conducted utilizing a chemical speciation computer model developed by the United States Geological Survey (USGS). The model used is a Microsoft Windows© interface for the newly released *PHREEQC* version 2.2 (Parkhurst and Appelo, 1999) entitled *PHREEQCI* (Charlton et al., 1997). The software allows for the input of the chemical characteristics of a given solution and then performs a speciation. The software also allows for the addition of a chemical reactant to the original solution to which a new speciation is performed. In this case, 10 mg of  $(NH_4)_2SO_4$  was added to the original solution and the speciation was then performed. Results from the speciation model reveals a decrease in the amount of complexation and ion pair formation as temperature increases (Figure 5). Figure 5 illustrates that as temperature increases the activity of  $NH_4SO_4^-$  decreases. This would indicate that at lower temperatures and early sample times the increase in the fraction of  $NH_4^+$ -N loss was due to complexation effects and not volatilization.

# Multi-Variate Regression Analysis

Multi-variate linear regression analysis was performed in an effort to identify water quality characteristics that may influence the loss of N through volatilization. Percent loss was regressed on the water quality data contained in Table 2. The technique used to accomplish this analysis was a backward elimination technique as outlined by the SAS Institute (1994). The final model retains only those variables that contribute significantly to the overall model. Variables found to contribute significantly to the overall model are found in Table 7 along with the parameter estimate and the OSL for that parameter. The most significant factor was temperature which was positively correlated with percent N loss along with electrical conductivity of the water ( $\text{EC}_w$ ) and carbonate concentration. Two variables that were negatively correlated and produced negative regression coefficients included pH and SO<sub>4</sub><sup>-</sup>-S concentrations. However, the ranges associated with the pH values encountered with these ten water sources was very small (8.1 – 8.6). Research investigating NH<sub>3</sub> volatilization in the past has clearly demonstrated a positive relationship between pH and NH<sub>3</sub> volatilization (Du Plessis and Kroontje, 1964).

The other variable for which a negative parameter estimate was calculated was  $SO_4^-S$ . This variable appeared to have a real effect on the rate of N loss through volatilization. As demonstrated in Figure 6, when the slope of the regression of percent loss as a function of temperature are plotted as a function of  $SO_4^-S$  concentration a negative relationship is observed. The relationship between decreasing rates of N loss through volatilization with increasing concentration of  $SO_4^-S$  is most likely due to an application of Le Chatelier's principle, or the "common ion effect", which predicts that a salt will be less soluble if one of its constituent ions is present in solution (Harris, 1991). As the concentration of  $SO_4^-S$  increases, the solubility of the  $(NH_4)_2SO_4$  decreases (eqn. 3), suppressing the free  $NH_4^+$  activity, which in turn reduces the potential for  $NH_3$  volatilization.

## **Conclusions**

The potential loss of fertilizer N placed in irrigation waters should be accounted for when making decisions about fertilizer N management. This is particularly true when considering the form of fertilizer being used. Potential losses may be greater under conditions where fertilizers are used containing high concentrations of free NH<sub>3</sub> or NH<sub>4</sub><sup>+</sup>. The converse must also be considered in that fertilizer used containing lower quantities of ammoniacal N (e.g. UAN32) would result in lower losses through volatilization. It was also observed that potential losses are much greater at temperatures above 35°C and may exceed 50% loss in the first 10-12 hours of application. Water quality appears to have an impact on NH<sub>3</sub> volatilization. In this study the higher concentrations of SO<sub>4</sub><sup>-</sup>S had an impact on reducing the amount of volatilization due to the decreased solubility of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. In general however, higher concentrations of total soluble salts (i.e.  $EC_w$ ) tended to increase the potential loss of N through volatilization.

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Table 1. Geographical location of sample for each of the 10 water sources.

Sample #	Sample Location (Elevation)	Source of Water
1	Yuma, AZ (32m)	Colorado River Water
2	Gila Bend, AZ (219m)	Gila River / Paloma Ranch Well Field
3	Buckeye, AZ (304m)	Roosevelt Irrigation District (RID)
4	Maricopa, AZ (361m)	Well water (Maricopa Agricultural Center – University of Arizona)
5	Maricopa, AZ (361m)	Colorado River Water (Maricopa-Stanfield Irrigation District - MSID)
6	Coolidge, AZ (422m)	San Carlos Irrigation District (SCID)
7	Marana, AZ (601m)	Well water (Marana Agricultural Center – University of Arizona)
8	Marana, AZ (601m)	Central Arizona Project - CAP (Colorado River Water)
9	Safford, AZ (901m)	Gila River Water
10	Safford, AZ (901m)	Well water (Safford Agricultural Center – University of Arizona)

Table 2. Water composition data for each of the 10 sources.

Sample	pН	Ca	Mg	Na	K	$CO_{3}^{2}$	HCO <sub>3</sub> <sup>-</sup>	Cľ	SO <sub>4</sub>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>2.</sup>	EC <sup>1</sup>	SAR <sup>2</sup>	SSP <sup>3</sup>	TSS <sup>4</sup>
						p	pm					ds/m			ppm
1	8.2	74	33	130	4.8	0	148.8	120	100	0.5	0.03	0.7	6.2	46.4	611
2	8.6	180	56	590	11.6	4.8	151.3	820	160	5.6	0.31	1.9	21.5	64.9	1981
3	8.3	42	29	250	8.7	1.2	185.4	340	48	3.8	0.14	1.0	13.7	69.8	909
4	8.4	220	40	330	4.9	1.2	102.5	420	230	16.4	0.06	1.5	11.1	49.9	1366
5	8.5	69	22	170	4.2	2.4	70.8	160	110	3.2	0.03	0.7	7.2	57.9	612
6	8.6	46	13	61	5.1	8.4	87.8	75	39	0.9	0.25	0.4	3.3	43.1	337
7	8.6	25	6	66	2.2	4.8	109.8	41	22	4.0	0.02	0.5	4.3	61.4	281
8	8.1	60	33	100	4.9	0	90.3	93	93	0.2	0.02	0.5	4.4	42.7	475
9	8.4	40	12	110	7.1	2.4	131.8	150	17	0.8	0.09	0.5	6.4	60.2	471
10	8.3	41	13	380	3.3	1.2	302.6	300	78	5.5	0.04	1.3	25.3	83.8	1125

1 Electrical conductivity of the solution

2 Sodium absorption ratio

3 Soluble sodium percentage

4 Total soluble salts

Table 3. Regression parameter estimates (slope) for data presented in Figure 3.

Source	Slope (Significant at $\alpha = 0.05$ )
Yuma (Colorado River)	3.204
Gila Bend (Gila River/Paloma Ranch)	3.592
Buckeye (RID)	3.786
Maricopa (well)	2.085
Maricopa (CAP)	3.515
Coolidge (SCID)	2.736
Marana (well)	3.992
Marana (CAP)	2.582
Safford (Gila River)	3.395
Safford (well)	3.252

Table 4. Analysis of variance and means separation by temperature for each water source.

	1	2	3	4	5	6	7	8	9	10
Source					Percent	Loss				
$40^{\circ}C$	89.6 a	88.5 a	94.7 a	73.5 a	83.0 a	86.4 a	91.0 a	88.6 a	86.4 a	90.4 a
35°C	68.5 b	64.2 b	77.9 b	56.1 b	52.9 b	60.2 b	65.4 b	59.3 b	70.1 b	74.8 b
30°C	53.2 c	53.5 c	61.9 c	46.2 c	34.7 c	54.3 c	45.1 c	54.1 c	39.7 c	53.6 c
25°C	41.3 d	32.2 d	36.9 d	42.1 d	30.7 c	42.8 d	31.2 d	47.4 d	41.3 c	43.4 d
SNK	2.8	1.6	1.7	3.5	4.5	3.6	6.4	3.2	3.7	4.3
OSL	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
C.V.	10.2	6.2	5.8	14.6	20.0	13.1	24.4	11.5	13.6	14.7

Table 5. Analysis of variance and means separation by water source at each temperature.

	Percent Loss						
Source	25°C	30°C	35°C	40°C			
Yuma (Colorado River)	41.3 ab*	53.2 b	68.5 c	89.6 cd			
Gila Bend (Gila River/Paloma Ranch)	32.2 c	53.5 b	64.2 d	88.5 d			
Buckeye (RID)	36.9 b	61.9 a	77.9 a	94.7 a			
Maricopa (well)	42.1 ab	46.2 c	56.1 f	73.5 g			
Maricopa (CAP)	30.7 c	34.7 e	52.9 g	83.0 f			
Coolidge (SCID)	42.8 ab	54.4 b	60.2 e	86.4 e			
Marana (well)	31.2 c	45.1 c	65.4 d	91.0 b			
Marana (CAP)	47.4 a	54.1 b	59.3 e	88.6 d			
Safford (Gila River)	41.3 ab	39.7 d	70.2 c	86.4 e			
Safford (well)	43.4 ab	53.6 b	74.8 b	90.4 bc			
SNK Critical Range	4.6	3.4	1.7	1.0			
Coefficient of Variation	26.4	15.6	5.9	2.7			
Observed Significance Level	0.0001	0.0001	0.0001	0.0001			

\* Means followed by the same letter are not significantly different according to an SNK means separation test.

Tuble 0. Regression and	Temperature	nates for fracti	Regression Parameter					
Source	°C	$\mathbf{r}^2$	ßg	ß	ß			
Yuma	25	0.2549	0.1890	0.0095				
1 01110	30	0.5236	0.1411	0.0161				
	35	0.8363	0.0523	0.0265				
	40	0.9552	0.0351	0.0377				
Gila Bend	25	0.2470	0.1228	0.0093				
	30	0.6262	0.1203	0.0173				
	35	0.9127	0.0225	0.0168	0.00038			
	40	0.9688	0.0208	0.0370				
Buckeye	25	0.1330	0.1836	0.0080				
-	30	0.6361	0.1343	0.0187				
	35	0.8465	0.0594	0.0157	0.00059			
	40	0.9826	0.0047	0.0629	-0.00097			
Maricopa (well)	25	0.1314	0.2369	0.0090				
	30	0.2125	0.1547	0.0127				
	35	0.5785	0.0734	0.0188				
	40	0.9585	-0.0150	0.0302				
Maricopa (CAP)	25	0.3254	0.1455	0.0104				
	30	0.5251	0.0592	0.0122				
	35	0.9083	0.0363	0.0075	0.00055			
	40	0.9718	0.0134	0.0288	0.00023			
Coolidge	25	0.3963	0.1788	0.0110				
-	30	0.2449	0.1804	0.0155				
	35	0.9590	0.0109	0.0187	0.00026			
	40	0.9708	0.0237	0.0353				
Marana (well)	25	0.3534	0.2076	0.0354	-0.00104			
	30	0.3077	0.1677	0.0126				
	35	0.7181	0.0914	0.0220				
	40	0.9733	-0.0168	0.0460	-0.00029			
Marana (CAP)	25	0.3962	0.1868	0.0137				
	30	0.1611	0.2925	0.0110				
	35	0.8883	0.0344	0.0123	0.00046			
	40	0.9758	0.0289	0.0363				
Safford (Gila River)	25	0.1592	0.2070	0.0082				
	30	0.8100	0.0611	-0.0072	0.00088			
	35	0.8828	0.0734	0.0256				
	40	0.9512	0.0358	0.0361				
Safford (well)	25	0.2125	0.2119	0.0111				
	30	0.6579	0.1125	0.0180				
	35	0.9551	-0.0270	0.0319				
	40	0.9604	0.0156	0.0551	-0.00075			

Table 6. Regression analysis parameter estimates for fraction of  $NH_4^+$ -N loss as a function of time.

\*All parameters listed are significant at the  $\alpha = 0.05$ 

	Variable	Parameter Estimate	OSL
β	Intercept	2.88630	0.00093
$\beta_1$	Temperature	0.03203	< 0.0001
$\beta_2$	pН	-0.40383	0.0033
$\overline{\beta_3}$	Carbonate	0.01728	0.0550
$\beta_4$	Electrical Conductivity	0.09883	0.0025
β <sub>5</sub>	Sulfate	-0.000755	0.0026



Figure 1. Total fractional loss of  $NH_4^+$ -N as a function of temperature for all water sources.



Figure 2. Fractional loss as a function of time for each of the four temperatures at locations A, Yuma Colorado River water; B, Gila Bend Gila River water plus Paloma Ranch well field; C, Buckeye RID water; and D, Maricopa well water.



Figure 3. Fractional loss as a function of time for each of the four temperatures at locations A, Maricopa CAP water; B, Coolidge SCID water; C, Marana well water; and D, Marana CAP water.



Figure 4. Fractional loss as a function of time for each of the four temperatures at locations A, Safford Gila River water; and B, Safford well water.



Figure 5. Activity of  $NH_4SO_4^-$  as a function of temperature for seven selected water sources.



Figure 6. Regression slopes from Table 3 plotted as a function of  $SO_4^{-}S$  concentrations.