

Temperature Quotients of Ammonia Emission of Different Nitrogen Sources Applied to Four Agricultural Soils

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Emission of N as NH_3 is the primary gaseous loss of N from N sources applied to soils. Knowledge of NH_3 volatilization, however, in relation to temperature is incomplete. Soils used in this study were a Biscayne marl soil (BMS) and Krome gravelly loam (KGL) from Florida, and Quincy fine sand (QFS) and Warden silt loam (WSL) soils from Washington. These soils were amended with either KNO_3 , NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, or urea, and incubated at 11, 20, or 29°C under 20 or 80% field capacity (FC) soil water regimes. A change in the rate of NH_3 emission corresponding to a 9°C change in temperature is expressed as the temperature quotient (Q_9), which describes the temperature effect on rates of NH_3 volatilization. At 20°C, the cumulative NH_3 emission at 20% FC was up to 8.1-fold greater than that at 80% FC. The Q_9 values of NH_3 emission from the WSL soil were up to 10-fold greater than those from the other three soils amended with either $(\text{NH}_4)_2\text{SO}_4$ or NH_4NO_3 . The Arrhenius activation energy (E_a) was about 188 J mol⁻¹ for the WSL soil but ≤42 J mol⁻¹ for the other soils. Volatilization from the WSL soil was highly temperature dependent. These results indicate that Q_9 and E_a could be used as indices for N management for crop production to minimize NH_3 emissions. Further research is needed, however, to verify the above relationships across a wide range of soils and agroclimatic regions.

Abbreviations: BMS, Biscayne marl soil; CAE, cumulative ammonia emission; FC, field capacity; IPAV, isothermal point of ammonia volatilization; KGL, Krome gravelly loam; QFS, Quincy fine sand; WSL, Warden silt loam.

Ammonia volatilization from applied N fertilizer significantly reduces the amount of ammoniacal N ($\text{NH}_3 + \text{NH}_4^+$) available for crop use, and can account for 50% of the N applied, depending on N sources (Fenn and Escarza, 1977; Wu et al., 2003). World agriculture is currently responsible for more than two-thirds of the global NH_3 input into the atmosphere (Bouwman, 1997). The emitted NH_3 gas can be transformed into N_2O that is a potent greenhouse gas with a direct global warming potential up to 295-fold greater than that of CO_2 (Energy Information Administration, 2005). Ammonia volatilization reduces N fertilizer efficiency and causes negative environmental implications.

Ammonia volatilization is a chemical reaction that is influenced by temperature, moisture, soil pH, type of fertilizer and its application rate, and other environmental factors (Fenn and Hossner, 1985). The soil solution NH_4^+ includes that from recently added fertilizer that is not adsorbed on soil particles. Soil temperature influences NH_4^+ absorption, conversion of NH_4^+ into NH_3 , and NH_3 emission (Fenn and Hossner, 1985;

International Fertilizer Industry Association, 2001). Fenn and Kissel (1974) reported that the influence of temperature on NH_3 losses from different fertilizers was greatest for NH_4NO_3 and least for $(\text{NH}_4)_2\text{SO}_4$. Ammonia losses from urea were quite similar to those from $(\text{NH}_4)_2\text{SO}_4$ in the temperature range from 12 to 32°C (Fenn and Miyamoto, 1981). Fenn and Escarza (1976) reported NH_3 losses of 8 and 16% of total applied N at 12 and 22°C, respectively, for Houston Black clay, and Harkey silty clay loam soils. As the temperature further increased to 30°C, the effect on NH_3 volatilization was negligible (Fenn and Escarza, 1976). Hence, temperature-induced effects on NH_3 volatilization were significant only in a narrow range of temperatures.

The temperature quotient (Q_{10}) is generally used to describe the effect of every 10°C increase in temperature on soil respiration (Winkler et al., 1996; Luo et al., 2001). Frank et al. (2002) modeled the effect of soil temperature to predict soil respiration. Similarly, Bunnell et al. (1977) modeled the influence of soil temperature and soil moisture on soil respiration. These models have been applied successfully to different ecosystems to describe the mechanisms of soil respiration (Heal, 1979; Frank et al., 2002). Also, a chemical reaction is closely related to energy acquisition for energy-consuming reactions or energy release for energy-producing reactions. Heat is one of the basic forms of energy and is associated with the motion of atoms or molecules such as gas emission. With respect to energy-consuming reactions, the higher the temperature, the faster a given chemical reaction will proceed. In 1889, Arrhenius developed an empirical equation, the Arrhenius equation, to quantify the temperature effects on the rate of reaction. Furthermore, the minimum amount of energy required to ensure that the reaction will occur is defined as Arrhenius activation energy (E_a). Information is limited

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and more research is needed to determine the effects of different temperature ranges on NH₃ emission from different N sources in different soil types.

It is useful to study NH₃ emission with regard to specific crop production systems. Potato (*Solanum tuberosum* L.) is not only an important crop in the Pacific Northwest but also a secondary crop in other regions of the USA, e.g., Florida. Research on NH₃ emissions is lacking from potato production in varied geographical regions. The state of Washington is the second largest producer of potatoes in the USA, after Idaho. The farm gate value of Washington potato production is about \$451 million. South-central Washington (Columbia Basin production region) is well known for the highest potato yields in the world, with yields of 60 to 80 Mg ha⁻¹. Quincy fine sand and Warden silt loam are typical soils used for potato production in this area. The soils are sandy and well drained. The growing period is characterized by long day lengths with little cloud cover, and high daytime air temperatures and cool nights. Since the annual precipitation is about 120 to 150 mm, potato production is dependent on irrigation. Unlike Washington, the main soils used for potato production in South Florida are Biscayne marl soil and Krome gravelly loam soil. The annual rainfall in South Florida ranges from 980 to 1651 mm. The recommended N rates for potato production in Washington and Florida are 330 kg N ha⁻¹ (Lang et al., 1999) and 200 kg N ha⁻¹ (Hutchinson et al., 2005), respectively. The average maximum temperature during the growing season from April to August in Washington is 2.7°C greater than that during the growing season from October to the following May in Florida. For the respective growing season, the minimum temperature in Washington is 6.7°C lower than that in Florida. The effects of different temperature ranges on NH₃ emission from different N sources have not been investigated in soils used for potato production. Specially, there is little information on increasing N-utilization efficiency of N fertilizers based on the effects of air temperature on NH₃ volatilization and a corresponding fertilization management strategy.

The objectives of this research were to: (i) estimate the temperature quotients of NH₃ emission from different N sources applied to different soils in the potato production regions in Florida and Washington; (ii) quantify the effects of different temperature ranges on NH₃ emission; and (iii) identify the Arrhenius activation energy of NH₃ emission from different fertilizer sources across different soil types, soil moisture levels, and incubation temperatures.

MATERIALS AND METHODS

Soils

Quincy fine sand (QFS; mixed, mesic Xeric Torripsamments) and Warden silt loam (WSL; coarse-silty, mixed, mesic, Xerollic Camborthids; a dark grayish-brown soil) were sampled (0–20-cm depth) from the Columbia Basin potato production region in south-central Washington. The typical soils used for potato production in South Florida are Biscayne marl soil (BMS; loamy, carbonatic, hyperthermic, shallow Typic Fluvaquents) and Krome gravelly loam (KGL; loamy-skeletal, carbonic, hyperthermic Lithic Udorthents). These two soils were collected from

Table 1. Principal chemical and physical properties of the soils used in the study.

Soilt	pH	Electrical conductivity µS cm ⁻¹	Organic matter g kg ⁻¹	Particle size distribution			Bulk density g cm ⁻³	Field capacity g kg ⁻¹	NH ₄ -N — mg N kg ⁻¹ —	NO ₃ -N
				Clay	Silt	Sand				
BMS	7.3	457	14.9	175	732	93	0.88	604.5	7.3	21.7
KGL	7.7	131	17.9	80	344	576	1.23	323.4	4.5	3.3
QFS	6.7	49	4.1	19	112	869	1.43	247.4	4.3	13.9
WSL	6.5	93	6.7	25	405	570	1.25	326.1	14.6	10.7

†BMS: Biscayne marl soil; KGL: Krome gravelly loam; QFS: Quincy fine sand; WSL: Warden silt loam.

commercial potato farms in South Florida. They were used for this study because there has been very little research on NH₃ emission from these soils when used for potato production. The principal chemical and physical properties of those soils are presented in Table 1.

Incubation Temperature

The incubation temperatures used were based on the mean air temperature in the selected production region during the crop growing season. In the Columbia Basin production region of Washington, the maximum and minimum air temperatures for the potato growing season are 29 and 11°C, respectively. These averages are based on 4 yr (2000–2003) of daily climatic data. This results in an average temperature of 20°C. In Florida, the high and low temperatures for the growing season from October to the following May are 26.5 and 18.4°C, respectively (NRCS, 1996).

Ammonia Trapping and Chemical Analysis

For each soil, 300 g (dry weight) was placed in a 500-mL incubation bottle. The soil surface area in the bottle was about 60 cm². The soil water content was adjusted to either 20 or 80% of field capacity (FC). The water contents at FC for the four soils were (v/w based on oven-dry soil): 604.5 ± 11.2 for the BMS; 323.4 ± 6.7 for the KGL; 247.4 ± 2.7 for the QFS; and 326.1 ± 2.8 mL kg⁻¹ for the WSL. One milliliter solution of N [as KNO₃, MH₄NO₃, (NH₄)₂SO₄, or urea] was uniformly applied on the soil surface with a micropipette. The amount of N applied was 45 mg N per bottle, equivalent to 75 kg N ha⁻¹ based on the soil surface area in the bottle. A treatment with deionized water was included as a control. Hence, there were 4 soils × 5 N sources (including the control) × 3 temperatures × 2 soil water regimes × 3 replications, which resulted in 360 total incubation bottles. Each incubation bottle was placed in a sealed plastic Ziploc storage bag (23 by 30 cm) and placed in an incubator adjusted to either 11, 20, or 29°C. A sponge spiked with the trapping solution was inserted into the mouth of the bottle to trap the volatilized NH₃. The sponge (about 5 cm in diameter) was cut from Yellow Flower Sponges (Arrow Plastic Manufacturing Co., Elk Grove Village, IL). Each cut sponge was spiked with 0.8 mL of trapping solution made by combining 35 mL concentrated H₃PO₄, 250 mL glycerol, and 715 mL deionized water (He et al., 1999). The sponge with the trapping solution was sampled at 1, 3, 7, 14, and 28 d and a new sponge (with the trapping solution) was placed to trap NH₃ for the subsequent incubation period. Ammonia in the sponges was extracted with 25 mL of 1 M KCl and measured using an Auto Analyzer III (Bran+Luebbe GmbH, Norderstedt, Germany) according to USEPA Method 350.1 (USEPA, 1993; Bran+Luebbe, 2003). The Statistical Analysis System (SAS) package, Version 9.1 (SAS Institute, 2007), was used to perform the statistical analyses.

Temperature Quotients of Ammonia Emission

To describe the quantitative relationship between the rate of a given chemical reaction and the temperature, Arrhenius in 1889 proposed an empirical equation, which is called the Arrhenius equation:

$$V = A \exp\left[-E_a/R(t + 273.15)\right] \quad [1]$$

where V is the reaction rate at temperature t (°C), R is the universal gas constant (8.314472 J °C⁻¹ mol⁻¹), A is the pre-exponential factor, and E_a is the Arrhenius activation energy of the reaction (J mol⁻¹). By differentiating Eq. [1], E_a can be defined as

$$E_a = R(t + 273.15)^2 \frac{d \ln V}{d(t + 273.15)} \quad [2]$$

Based on Eq. [1] and [2] (Johnson et al., 1954; Raison, 1980), the changes in the rate of NH₃ volatilization with temperature can be quantitatively expressed as follows:

$$\ln\left(\frac{V_1}{V_2}\right) = \left(\frac{E_a}{R}\right) \left(\frac{1}{t_2 + 273.15} - \frac{1}{t_1 + 273.15}\right) \quad [3]$$

where V_1 and V_2 are the maximum rates of the NH₃ volatilization at temperatures t_1 and t_2 (°C), respectively, and E_a is the Arrhenius activation energy (J mol⁻¹). The activation energy is the amount of energy required to ensure that NH₃ volatilization occurs. Accordingly, a change in the rate of NH₃ volatilization corresponding to a 10°C change in temperature is expressed as the temperature quotient (Q_{10}). During the potato growing season in Washington, the temperature interval between the mean maximum and the daily mean and mean minimum are 9°C. Therefore, the temperature quotient for NH₃ emission in this research is defined as

$$Q_9 = \frac{V_1/V_2}{(t_1 - t_2)/9} \quad [4]$$

where t_1 and t_2 are the temperatures corresponding to the V_1 and V_2 rates, respectively.

Using Eq. [4], temperature quotients for the range of temperature from 11 to 20 and 20 to 29°C were calculated for NH₃ emissions from the four soils amended with (NH₄)₂SO₄, NH₄NO₃, KNO₃, and urea and incubated at either 20 or 80% FC.

Active Temperature Quotients of Ammonia Emission

Equation [4] shows that $Q_9 \geq 0$; therefore, Q_9 can indicate the quantity (intensity) of change in NH₃ emission between the two temperature ranges, but it does not show the quality (direction, i.e., increase or decrease) of the change. Based on the temperature quotient (Q_9), the active temperature quotient (AQ₉) of NH₃ emission is further defined as

$$AQ_9 = \frac{(V_1 - V_2)/V_2}{(t_1 - t_2)/9} \quad [5]$$

While the meaning of V_1 , V_2 , t_1 , and t_2 are identical to those in Eq. [4], the values of AQ₉ can be either >0 when $V_1 > V_2$, <0 when $V_2 > V_1$, or 0 when $V_1 = V_2$. Therefore, AQ₉ can readily indicate both the quantity and quality of the change in emission rate with temperature.

The Arrhenius activation energy (E_a) is the amount of energy required to ensure that a chemical reaction occurs. Ammonia volatilization is a chemical reaction described by Eq. [3] and [4]. Based on these two equations, the relationship between E_a and Q_9 can be described as

$$E_a = 2.303R \left[\frac{(t + 273.15)^2 + 9(t + 273.15)}{9} \right] \log_{10} Q_9 \quad [6]$$

where t is temperature (°C) and Q_9 is the temperature quotient as described above in Eq. [1] and [4]. Since Q_9 is known, E_a can be calculated for various conditions using Eq. [6].

RESULTS

Cumulative Ammonia Emission

The average cumulative NH₃ emission (CAE) across all soils, temperatures, and moisture regimes was 5787, 7461, 3010 g N ha⁻¹ for (NH₄)₂SO₄, urea, and NH₄NO₃, respectively. This indicated that the average CAE from NH₄NO₃ was about half that of either (NH₄)₂SO₄ or urea because the amount of NH₄⁺ in a mole of NH₄NO₃ is about 50% of that in a mole of either (NH₄)₂SO₄ or urea. The CAE was as high as 19,283 g N ha⁻¹ from the KGL soil amended with 75,000 g N ha⁻¹ (Table 2). The CAE for a given source, particularly the NH₄⁺ form or a source that transforms into the NH₄⁺ form, amended to the Florida soils was much higher than from the same N source amended to the Washington soils, with a few exceptions. For example, the average CAEs were 7306, 7949, 3680, and 2862 g N ha⁻¹ for the BMS, KGL, QFS, and WSL soils, respectively, across all temperatures, water regimes, and N sources except KNO₃. The corresponding CAEs for KNO₃ were 123, 68, 62, and 42 g N ha⁻¹. At 20% FC, the maximum ranges in the CAE values from (NH₄)₂SO₄ were 20.7-fold between the BMS and WSL soils at 11°C, 10.0-fold at 20°C between the KGL and QFS soils, and 15.9-fold at 29°C also between the KGL and QFS soils. The mean CAE values across all incubation temperatures at 20% FC showed a 5.9-fold difference among the four soils. The corresponding value at 80% FC soil water regime was 4.2-fold. The effect of soil water regime on the CAE from (NH₄)₂SO₄ was least in the QFS soil. Among the other three soils, the increases in CAE at 20% FC, compared with 80% FC, were 2.4- to 4.7-, 4.1- to 8.1-, and 2.5- to 4.7-fold at 29, 20, and 11°C, respectively. This disparity in NH₃ emission rates is partially due to the higher pH of the Florida soils than the Washington soils. The soil moisture regime played an important role in determining the magnitude of volatilization losses from different sources of N. The soil water regime is also important for dissolution of the NH₄⁺ source applied to the soil surface and for the transfer of dissolved NH₄⁺ ions deep into the soil profile, where they may be adsorbed. Ammonia emission was almost negligible in the unamended soil or in the soil amended with KNO₃ (Table 2).

Temperature Quotients of Ammonia Emission

In the WSL soil at 20 to 29°C, the Q_9 for NH₃ emission from (NH₄)₂SO₄ was 10 on Day 1, but declined to 2.5 by Day 14 (Fig. 1). This decline in emission rate could probably be attributed to a rapid depletion of NH₄⁺ with time. Rapid volatilization of NH₃ occurs in this soil at 29°C, leading to a reduction in the amount of available NH₄⁺. In the 20 to 29°C temperature range, the Q_9 was much higher in the WSL soil than the other three soils; however, this was not the case in the 11 to 20°C temperature range.

Mean Q_9 values for NH₃ emissions from (NH₄)₂SO₄ amended to the KGL soil at 11 to 20°C were about 0.5- to 5.2-fold higher than those at 20 and 80% FC, respectively, at 20 to 29°C. Mean

Q_9 values for the KGL soil at 20 and 80% FC were 0.9 and 0.2 at 20 to 29°C, and 1.4 and 1.5 at 11 to 20°C, respectively. The corresponding values in the QFS soil were 0.9 and 0.5 at 20 to 29°C, and 1.3 and 1.0 at 11 to 20°C. Thus, in the case of the KGL and QFS soils, the temperature effect on NH_3 volatilization was greater with an increase in temperature at 11 to 20°C than at 20 to 29°C.

The Q_9 values for NH_3 emissions from urea across two different temperature ranges and soil water regimes were quite different from those for either $(NH_4)_2SO_4$ or NH_4NO_3 (Fig. 1–3). In the 20 to 29°C temperature range at 20% FC, on Day 1, the Q_9 values for urea in all the soils were 1 to 2. At 20% FC and the 11 to 20°C temperature range, the Q_9 values were close to 4.0 for the QFS and WSL soils, while the Q_9 values for the BMS and KGL soils were 1.0 to 1.5.

Most of the Q_9 values of NH_3 emissions from the soil amended with KNO_3 were greater at 20% FC than at 80% FC in the 11 to 20°C temperature range (Fig. 4). At 80% FC, the Q_9 values were lower at 11 to 20°C than those at 20 to 29°C.

Figure 5 shows the Q_9 values for the unamended soils. At either 11 to 20 or 20 to 29°C, the Q_9 values at 20% FC were >1.0 before Day 14 but <1.0 after Day 14. These changes in the Q_9 values can probably be attributed to the decrease in the availability of NH_4^+ in the soils with time.

Based on the calculations from the CAEs (Table 2), the average rates of NH_3 emission were only 1.2 to 2.1 g N ha⁻¹ for the control and 1.5 to 4.4 g N ha⁻¹ for KNO_3 across all temperatures and water regimes. Hence, the following discussion is focused on the NH_3 emission results from the $(NH_4)_2SO_4$, urea, and NH_4NO_3 sources.

Active Temperature Quotients of Ammonia Emission

According to Eq. [5], the AQ_9 can be either ≥ 0 or ≤ 0 . The variation in AQ_9 values can be attributed to differential responses of soils to the incubation temperatures. The AQ_9 values shown in Fig. 6 through 8 indicate the magnitude as well as the direction (increase or decrease) in N loss. The AQ_9 values for the WSL soil were as high as 9.3; however, those for the BMS, KGL, and QFS soils were either negative or <2 except that from the BMS soil on Day 14 at 20 to 29°C (Fig. 6 and 7). These AQ_9 values suggest that NH_3 volatilization from the WSL soil was very temperature dependent in the 20 to 29°C range when $(NH_4)_2SO_4$ and NH_4NO_3 were used (Fig. 6 and 7). The temperature dependency

Table 2. Cumulative NH_3 emission following addition of N fertilizers during 28 d of incubation at three temperatures and soil water regimes of 20 or 80% of field capacity (FC).

Soil†	Cumulative NH_3 emission							
	20% FC				80% FC			
	29°C	20°C	11°C	Average	29°C	20°C	11°C	Average
	g N ha ⁻¹							
	<u>$(NH_4)_2SO_4$</u>							
BMS	12,019 B‡	13,630 B	16,633 A	14,094	2556 B	2699 B	6,406 A	3887
KGL	17,819 A	19,283 A	15,101 B	17,401	5027 A	4715 A	3,197 B	4313
QFS	1,771 D	1,213 C	1,680 C	1,554	1047 C	1041 C	1,055 C	1048
WSL	6,036 C	2,050 C	804 C	2,963	2527 B	254 D	321 D	1034
	<u>Urea</u>							
BMS	9,469 B	7,981 C	17,158 A	11,536	2527 B	3413 B	10,852 A	5597
KGL	12,622 A	18,169 A	9,255 C	13,349	2603 B	2336 C	1,671 C	2203
QFS	12,255 A	11,886 B	11,445 B	11,862	6323 A	4265 A	4,714 B	5101
WSL	8,024 B	7,892 C	9,102 C	8,340	2438 B	1309 D	1,344 C	1697
	<u>NH_4NO_3</u>							
BMS	4,928 C	6,942 B	7,214 A	6,361	1240 C	1155 B	4,692 A	2363
KGL	9,032 A	9,817 A	5,950 B	8,266	2793 A	2247 A	1,456 B	2165
QFS	1,342 D	1,607 C	876 C	1,275	1640 B	1165 B	908 C	1238
WSL	6,347 B	1,047 C	587 D	2,660	1093 C	157 C	189 D	480
	<u>KNO_3</u>							
BMS	129 A	99 A	126 A	118	46 B	30 C	306 A	127
KGL	82 B	98 A	39 C	73	57 A	62 A	71 B	63
QFS	71 B	61 B	61 B	64	54 A	50 B	73 B	59
WSL	35 C	35 C	58 B	42	46 B	27 C	54 C	42
	<u>Control (unfertilized)</u>							
BMS	26 A	29 B	47 A	34	37 AB	32 A	187 A	85
KGL	28 A	20 C	45 A	31	32 B	18 B	65 C	38
QFS	26 A	29 B	53 A	36	40 A	34 A	59 C	44
WSL	25 A	35 A	34 B	31	40 A	33 A	83 B	52

†BMS: Biscayne marl soil; KGL: Krome gravelly loam; QFS: Quincy fine sand; WSL: Warden silt loam.

‡Means followed by different letters within columns are significantly different at $P = 0.05$ for each N source, each soil water regime, and each incubation temperature.

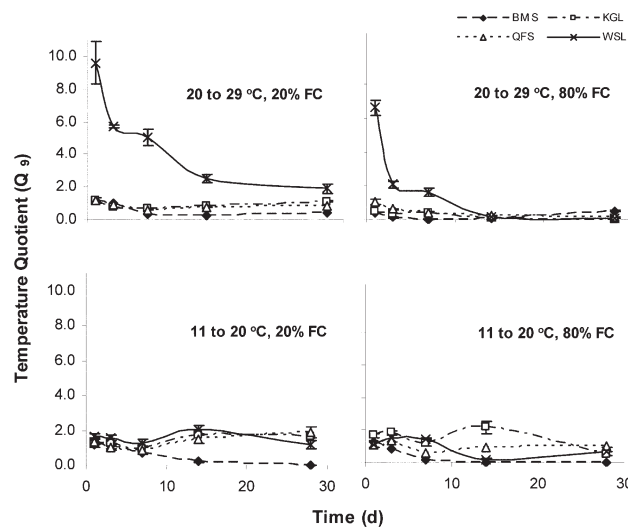


Fig. 1. The temperature quotients (Q_9 , the change in the rate of NH_3 emission corresponding to a 9°C change in temperature) for NH_3 emissions from four soils amended with $(NH_4)_2SO_4$ at soil water regimes of either 20 or 80% of field capacity (FC). BMS: Biscayne marl soil; KGL: Krome gravelly loam; QFS: Quincy fine sand; WSL: Warden silt loam.

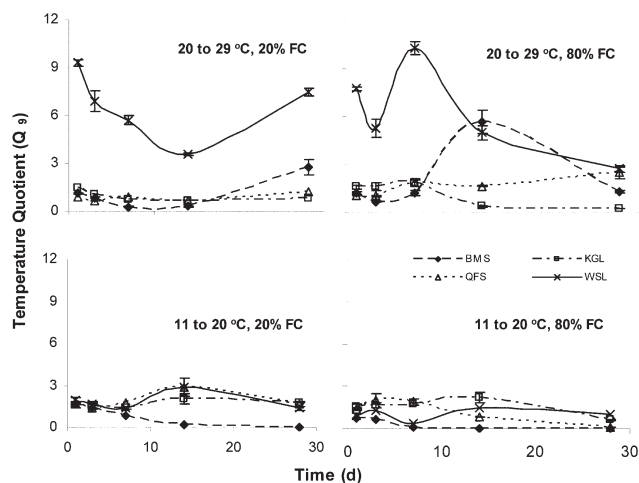


Fig. 2. The temperature quotients (Q_9 , the change in the rate of NH_3 emission corresponding to a 9°C change in temperature) for NH_3 emissions from four soils amended with NH_4NO_3 at soil water regimes of either 20 or 80% of field capacity (FC). BMS: Biscayne marl soil; KGL: Krome gravelly loam; QFS: Quincy fine sand; WSL: Warden silt loam.

of NH_3 emission, however, was not evident at 11 to 20°C across all soils evaluated in this study.

The NH_3 emission from urea involves different reactions than those for NH_3 emission from $(\text{NH}_4)_2\text{SO}_4$ or NH_4NO_3 . At 20% FC, all of the AQ_9 values for NH_3 emission from urea-amended soils were <1 in all soils except the KGL soil at either 11 to 20 or 20 to 29°C after Day 3 (Fig. 8). At 80% FC and 20 to 29°C , the AQ_9 values for NH_3 emission from urea applied to the BMS and WSL soils increased to almost 3 on Day 28. In contrast, the AQ_9 values for the KGL and QFS soils steadily declined and became zero or

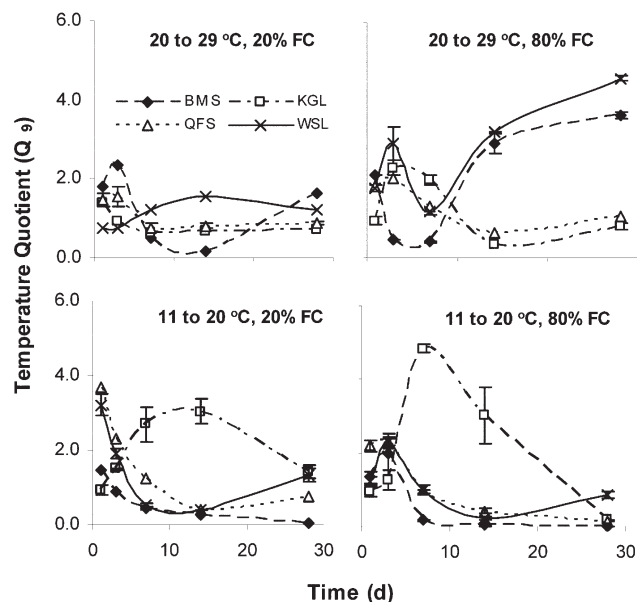


Fig. 3. The temperature quotients (Q_9 , the change in the rate of NH_3 emission corresponding to a 9°C change in temperature) for NH_3 emissions from four soils amended with urea at soil water regimes of either 20 or 80% of field capacity (FC). BMS: Biscayne marl soil; KGL: Krome gravelly loam; QFS: Quincy fine sand; WSL: Warden silt loam.

negative after Day 14. At 80% FC and 11 to 20°C , the AQ_9 values for the BMS, WSL, and QFS soils were about 1 in the first 3 d but <0 after Day 7. Under these conditions, the AQ_9 values for the KGL soil were 3.9 on Day 7 and 2.0 on Day 14. Ammonia emission from urea applied to different soils is complicated by various chemical reactions including enzymatic and volatilization reactions. The effect of a change in temperature on NH_3 emission decreased with time because an AQ_9 value of zero suggests that there was no effect of changing temperature. This was true in most cases toward the latter half of the incubation duration except for the WSL and BMS soils incubated at 20 to 29°C and 80% FC.

The differences in AQ_9 for NH_3 emission from urea applied to different soils were much smaller than those from either $(\text{NH}_4)_2\text{SO}_4$ or NH_4NO_3 (Fig. 6–8) due to the lag time required for transformation of urea into the NH_4^+ form, which can be volatilized. This transformation requires the presence of the urease enzyme. Enzymatic lysis of urea by urease is the critical step for NH_3 volatilization from urea.

DISCUSSION

The Arrhenius Activation Energy of Ammonia Volatilization

The E_a values for different soils amended with either $(\text{NH}_4)_2\text{SO}_4$ or NH_4NO_3 were calculated at 15.5 and 24.5°C , which represent the midpoint of the 11 to 20 and 20 to 29°C temperature ranges (Fig. 9). The E_a value for the QFS soil amended with NH_4NO_3 at 24.5°C was negative because the NH_3 emission rate for this soil was lower at 20 to 29°C than that at 11 to 20°C .

The variation in E_a values among different soils would indicate differences in NH_4^+ desorption potential of the soils. At 24.5°C , the E_a value for the WSL soil with either an $(\text{NH}_4)_2\text{SO}_4$ or NH_4NO_3 source of N was consistently greater than for the other three soils. This may be attributed, in part, to the WSL soil having the lowest pH among the four soils evaluated in this study (Table 1). Lower pH facilitates maintaining NH_4^+ ions in the soil solution for a longer period of time, which favors decreased NH_3 volatilization. Dynamic equilibrium between NH_4^+ and NH_3 in the soil solution is described as follows:



$$K_a = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} \quad [8]$$

where K_a is the acid dissociation constant of NH_4^+ . Furthermore, Eq. [8] may be written in logarithmic form:

$$\log_{10} K_a - \log_{10} [\text{H}^+] = \log_{10} \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \quad [9]$$

Since $-\log_{10}[\text{H}^+]$ is the pH and $-\log_{10}K_a$ is the $\text{p}K_a$, the following equation describes the relationship between NH_3 and NH_4^+ at a given pH:

$$\log_{10} \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = \text{pH} - \text{p}K_a \quad [10]$$

Therefore, the NH_3 to NH_4^+ ratio was 1:617 ($\text{p}K_a = 9.25$) for the WSL soil with a pH of 6.46. The corresponding ratio was 1:36 for the KGL soil with a pH of 7.69. Based on this, the

activation energy of the KGL soil was much lower than that of the WSL soil. Ammonium adsorption involves two forces (Clark, 1974): (i) a chemical force (chemisorption), which requires a strong force involving a combination of covalent (electron sharing) bonding; and (ii) a physical force (physical adsorption), which requires a weak force, for example Van der Waals bonding (Sparks, 1995). The ionized NH_3 (i.e., NH_4^+) is really adsorbed by soil particles via strong bonds. Desorption of NH_4^+ adsorbed via chemisorption requires much more energy than that adsorbed via physical adsorption.

The E_a for desorption of NH_4^+ from soil particles is low when surface functional groups in soils are occupied by other ions. Electrical conductivity of the BMS soil was five-fold greater than that of the WSL soil (Table 1). This suggests an abundance of different ions occupying the functional groups on the BMS soil particles, resulting in fewer surface functional groups available for NH_4^+ adsorption. In contrast, the WSL soil with low electrical conductivity provides a greater amount of surface functional groups available for NH_4^+ adsorption. This may explain, in part, the greater energy required for NH_3 emission from applied $\text{NH}_4^+\text{-N}$ from the WSL soil than from the BMS. In soils where a large proportion of ions other than NH_4^+ occupy the free functional groups (for example, the BMS, Table 1), or in soils with an inherently low density of surface functional groups, a greater amount of NH_4^+ is maintained in the soil solution due to a low proportion of NH_4^+ being adsorbed by the soil particles. Hence, the free NH_4^+ ions are readily volatilized compared with NH_4^+ ions that are adsorbed.

At 11 to 20°C, the E_a was greater for NH_4NO_3 than for $(\text{NH}_4)_2\text{SO}_4$ in all four soils (Fig. 9). This may suggest that the NH_4^+ ions from NH_4NO_3 were adsorbed by a force stronger than that required for the absorption of NH_4^+ ions derived from $(\text{NH}_4)_2\text{SO}_4$ because NH_4NO_3 yields only half as many NH_4^+ ions as $(\text{NH}_4)_2\text{SO}_4$, and this half quantity of NH_4^+ ions derived from NH_4NO_3 may be sufficient to just occupy the functional groups

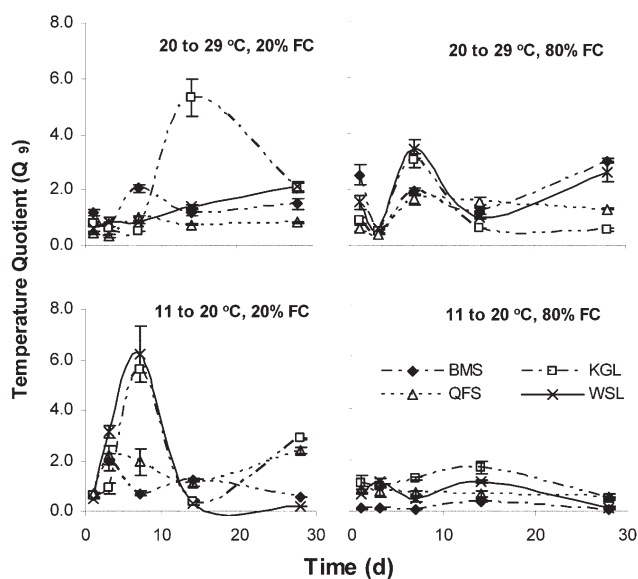


Fig. 4. The temperature quotients (Q_9 , the change in the rate of NH_3 emission corresponding to a 9°C change in temperature) for NH_3 emissions from four soils amended with KNO_3 at soil water regimes of either 20 or 80% of field capacity (FC). BMS: Biscayne marl soil; KGL: Krome gravelly loam; QFS: Quincy fine sand; WSL: Warden silt loam.

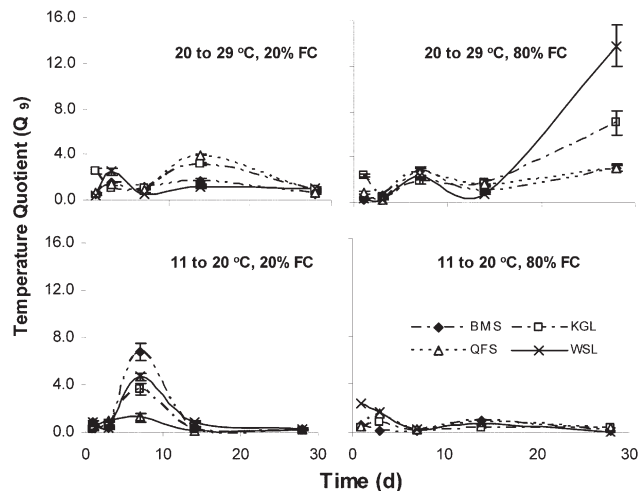


Fig. 5. The temperature quotients (Q_9 , the change in the rate of NH_3 emission corresponding to a 9°C change in temperature) for NH_3 emissions from four soils unamended with any fertilizers at soil water regimes of either 20 or 80% of field capacity (FC). BMS: Biscayne marl soil; KGL: Krome gravelly loam; QFS: Quincy fine sand; WSL: Warden silt loam.

via chemisorption. The results of this study suggest that application of NH_4^+ at high rates would result in high NH_3 emissions due to the presence of NH_4^+ ions far exceeding the adsorption capacity of the soil, especially those functional groups via chemisorption.

Isothermal Point of Ammonia Volatilization

Using the AQ_9 curves, we can estimate the duration required for similar amounts of NH_3 emission from different N fertilizer sources. The point of intersection of AQ_9 curves with the x axis is called the *isothermal point of ammonia volatilization* (IPAV). Based on this criterion, the AQ_9 curves in this study could be classified into two different groups: (i) those with or (ii) those without an IPAV (Fig. 6–8). Those with an IPAV, whose AQ_9 values were in a range from 1.0 to -1.0, were not sensitive to temperature

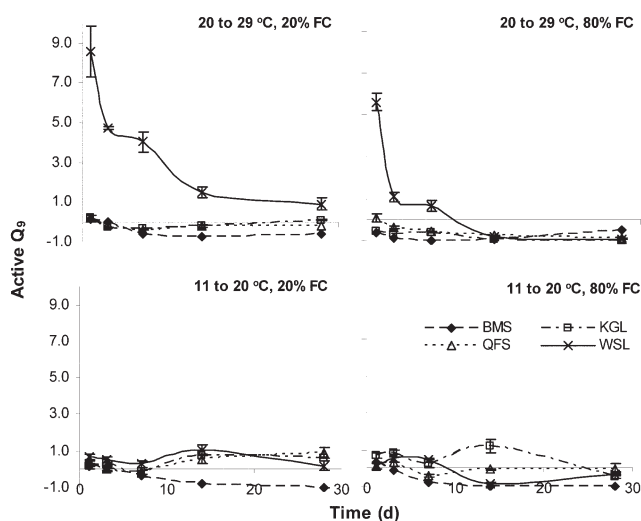


Fig. 6. The active temperature quotients (AQ_9) of NH_3 emission rates from the four soils amended with $(\text{NH}_4)_2\text{SO}_4$ at soil water regimes of either 20 or 80% of field capacity (FC). BMS: Biscayne marl soil; KGL: Krome gravelly loam; QFS: Quincy fine sand; WSL: Warden silt loam.

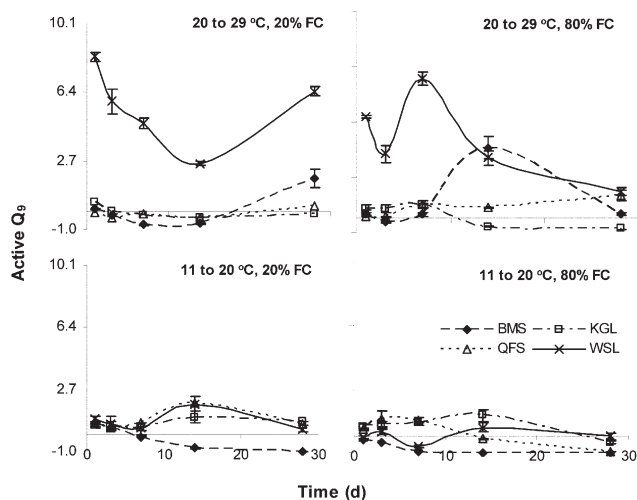


Fig. 7. The active temperature quotients (AQ_9) of NH_3 emission rates from four soils amended with NH_4NO_3 at soil water regimes of either 20 or 80% of field capacity (FC). BMS: Biscayne marl soil; KGL: Krome gravelly loam; QFS: Quincy fine sand; WSL: Warden silt loam.

increases, i.e., their curves just meandered about the x axis when the soil was incubated at different temperatures. The AQ_9 curves of the BMS, KGL, and QFS soils belong to this group. Those with or without an IPAV and with AQ_9 values >1.0 were temperature sensitive, however, since those curves could be far away from the x axis and changed greatly as the incubation temperature increased. For example, the IPAV for the WSL soil amended with $(NH_4)_2SO_4$ occurred after Day 7 in the 20 to 29°C temperature range and 80% FC (Fig. 6); however, the AQ_9 curve for the same soil didn't have an IPAV in the same temperature range at 20% FC. This implies that the FC of the soil influenced the temperature dependency of NH_3 emission. The IPAVs for the BMS soil occurred early in the incubation under most conditions (Fig. 6–8). The figures show that the rates of NH_3 emission from the BMS soil in the 20 to 29°C range were higher than those at 11 to 20°C at both 20 and 80% FC only in the first 3 d during incubation.

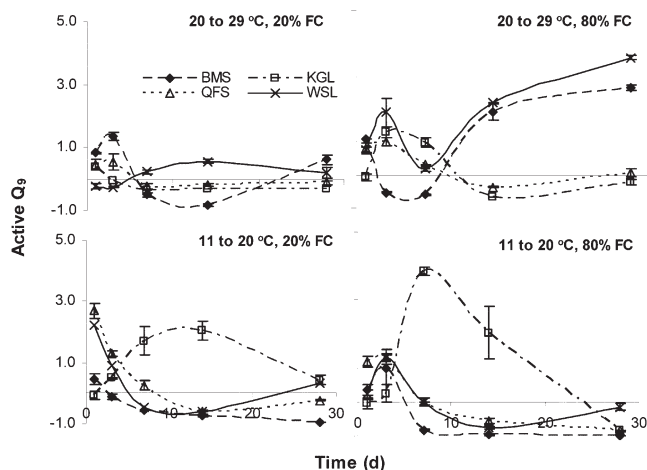


Fig. 8. The active temperature quotients (AQ_9) of NH_3 emission rates from four soils amended with urea at soil water regimes of either 20 or 80% of field capacity (FC). BMS: Biscayne marl soil; KGL: Krome gravelly loam; QFS: Quincy fine sand; WSL: Warden silt loam.

After that, the rates were even lower in the 20 to 29°C range than those at the corresponding lower temperatures. This implies that the effects of temperature on NH_3 emission rates were basically negative, even though they seemed slightly positive at the beginning. Thus the initially higher rates of NH_3 emission might not be due to temperature but to the abundance of NH_4^+ ions present.

Importance of the Arrhenius Activation Energy and the Isothermal Point of Ammonia Volatilization

The above indices suggest that the properties of the tested soils were very different in NH_4^+ adsorption and, hence, the NH_3 emission rates differed greatly. This may provide important insight into N fertilizer management aimed at reduction of N_2O emissions (Sutton et al., 1998). About 4% of the globally emitted NH_3 can be oxidized by OH radicals and NO_2 (Finlayson-Pitts and Pitts, 2000). A fraction of the oxidized NH_3 is transformed to N_2O and this can constitute 5% of the global N_2O emission (Ferm, 1998). Both E_a and IPAV suggested that the NH_3 emission from the WSL soil was temperature sensitive, unlike that from the BMS, KGL, and QFS soils. This indicates that the N available for crop uptake may be greater if N fertilizer was applied to the WSL soil in a cooler season; however, the timing of N application would have negligible effects on NH_3 volatilization in the BMS, KGL, and QFS soils. Further research is needed to apply these new concepts of E_a or IPAV in relation to NH_3 emissions from different N sources across a wide range of soils and agroclimatic zones to develop a database and guidelines to use these concepts for N management to minimize gaseous losses and to enhance N uptake efficiency.

CONCLUSIONS

The Q_9 and AQ_9 terms for NH_3 emission were introduced to describe the relationship between the rate of NH_3 emission and changes in temperature. Unlike the Q_9 , which represents only the qualitative relationship, the AQ_9 describes the qualitative and quantitative relationship between NH_3 emission and temperature. The E_a is the Arrhenius activation energy for desorption of the NH_4^+ ion from soil particles. This study demonstrated that, among the four soils evaluated, the temperature dependence of NH_3 emission was significant only in the WSL soil. The soil factors affecting the transformation and losses of N should be considered in determining fertilizer regimes for different crops grown on different soils. Ammonia emission from either NH_4NO_3 or $(NH_4)_2SO_4$ amended to the

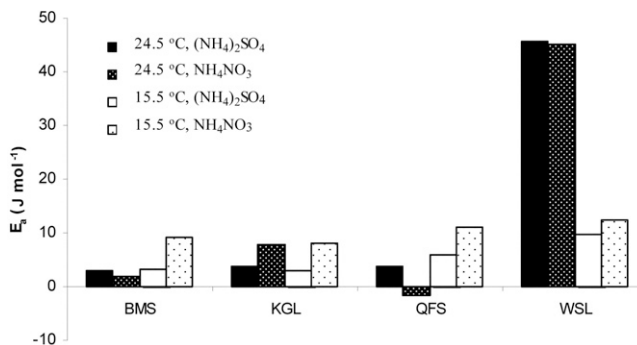


Fig. 9. The Arrhenius activation energy (E_a) of NH_3 emission for four soils amended with either $(NH_4)_2SO_4$ or NH_4NO_3 at a soil water regime of 20% of field capacity (FC). BMS: Biscayne marl soil; KGL: Krome gravelly loam; QFS: Quincy fine sand; WSL: Warden silt loam.

WSL soil was greater at >20°C than at lower temperatures. This study revealed that the Q_{10} values for the WSL soil ranged up to 10 with $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 at 20 to 29°C at either 20 or 80% FC. Overall, the E_a and IPAV can provide important insight into the dynamics of NH_3 emission from different N sources as influenced by the agroclimatic and soil factors. Further research is needed, however, to verify these relationships across a wide range of soils and environmental conditions.

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