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

G. D. Liu
Y. C. Li*
Soil and Water Science Dep.
Tropical Research and Education Center
Univ. of Florida
18905 SW 280th St.
Homestead, FL 33031

A. K. Alva
USDA-ARS
24106 N. Bunn Rd.
Prosse, WA 99350

Emission of N as NH₃ is the primary gaseous loss of N from N sources applied to soils. Knowledge of NH₃ 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 KNO₃, NH₄NO₃, (NH₄)₂SO₄, 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 NH₃ emission corresponding to a 9°C change in temperature is expressed as the temperature quotient (Qₙ), which describes the temperature effect on rates of NH₃ volatilization. At 20°C, the cumulative NH₃ emission at 20% FC was up to 8.1-fold greater than that at 80% FC. The Qₙ values of NH₃ emission from the WSL soil were up to 10-fold greater than those from the other three soils amended with either (NH₄)₂SO₄ or NH₄NO₃. The Arrhenius activation energy (Eₐ) 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 Qₙ and Eₐ could be used as indices for N management for crop production to minimize NH₃ 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 (NH₄ + NH₃⁺) available for crop use, and can account for 50% of the N applied, depending on N sources (Fenn and Escarzaga, 1977; Wu et al., 2003). World agriculture is currently responsible for more than two-thirds of the global NH₃ input into the atmosphere (Bouwman, 1997). The emitted NH₃ gas can be transformed into N₂O that is a potent greenhouse gas with a direct global warming potential up to 295-fold greater than that of CO₂ (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 NH₃⁺ includes that from recently added fertilizer that is not adsorbed on soil particles. Soil temperature influences NH₃⁺ absorption, conversion of NH₃⁺ into NH₃, and NH₃ emission (Fenn and Hossner, 1985; International Fertilizer Industry Association, 2001). Fenn and Kissel (1974) reported that the influence of temperature on NH₃ losses from different fertilizers was greatest for NH₄NO₃ and least for (NH₄)₂SO₄. Ammonia losses from urea were quite similar to those from (NH₄)₂SO₄ in the temperature range from 12 to 32°C (Fenn and Miyamoto, 1981). Fenn and Escarzaga (1976) reported NH₃ 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 NH₃ volatilization was negligible (Fenn and Escarzaga, 1976). Hence, temperature-induced effects on NH₃ volatilization were significant only in a narrow range of temperatures.

The temperature quotient (Qₙ₀) 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 (Eₐ). Information is limited...
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 27°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.

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

<table>
<thead>
<tr>
<th>Soil†</th>
<th>pH</th>
<th>Electrical conductivity</th>
<th>Organic matter</th>
<th>Particle size distribution</th>
<th>Bulk density</th>
<th>Field capacity</th>
<th>NH₃−N</th>
<th>NO₃−N</th>
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</thead>
<tbody>
<tr>
<td>BMS</td>
<td>7.3</td>
<td>457</td>
<td>14.9</td>
<td>175 732 93</td>
<td>0.88</td>
<td>604.5</td>
<td>7.3</td>
<td>21.7</td>
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<tr>
<td>KGL</td>
<td>7.7</td>
<td>131</td>
<td>17.9</td>
<td>80 344 576</td>
<td>1.23</td>
<td>323.4</td>
<td>4.5</td>
<td>3.3</td>
</tr>
<tr>
<td>QFS</td>
<td>6.7</td>
<td>49</td>
<td>4.1</td>
<td>19 112 869</td>
<td>1.43</td>
<td>247.4</td>
<td>4.3</td>
<td>13.9</td>
</tr>
<tr>
<td>WSL</td>
<td>6.5</td>
<td>93</td>
<td>6.7</td>
<td>25 405 570</td>
<td>1.25</td>
<td>326.1</td>
<td>14.6</td>
<td>10.7</td>
</tr>
</tbody>
</table>

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

MATERIALS AND METHODS

Soils

Quincy fine sand (QFS; mixed, mesic Xeric Torripsamments) and Warden silt loam (WSL; coarse-silty, mixed, mesic, Xerolic 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 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, NH₄NO₃, (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 replicates, 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:

\[ V = A \exp\left[-\frac{E_a}{R} \left(\frac{t}{t + 273.15}\right)\right] \]  

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

\[ E_a = R \left(\frac{t + 273.15}{t + 273.15}\right) d \ln V \left(\frac{t + 273.15}{t + 273.15}\right) \]  

Based on Eq. [1] and [2] (Johnson et al., 1954; Raison, 1980), the changes in the rate of NH\(_3\) volatilization with temperature can be quantitatively expressed as follows:

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

where \( V_1 \) and \( V_2 \) are the maximum rates of the NH\(_3\) 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 NH\(_4\) volatilization occurs. Accordingly, a change in the rate of NH\(_3\) volatilization corresponding to a 10°C change in temperature is expressed as the temperature quotient (\( Q_9 \)). 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 NH\(_3\) emission in this research is defined as

\[ Q_9 = \frac{V_1}{V_2} \left(\frac{t_1 - t_2}{9}\right) \]  

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 NH\(_3\) emissions from the four soils amended with (NH\(_4\))\(_2\)SO\(_4\), NH\(_4\)NO\(_3\), KNO\(_3\), 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 NH\(_3\) 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 (AQ\(_9\)) of NH\(_3\) emission is further defined as

\[ \text{AQ}_9 = \frac{(V_1 - V_2)/V_2}{(t_1 - t_2)/9} \]  

While the meaning of \( V_1, V_2, t_1, \) and \( t_2 \) are identical to those in Eq. [4], the values of AQ\(_9\) can be either >0 when \( V_1 > V_2 <0 \) when \( V_2 > V_1 \), or 0 when \( V_1 = V_2 \). Therefore, AQ\(_9\) 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

\[ E_a = 2.303R \left[ \frac{(t + 273.15)^3 + 9(t + 273.15)}{9} \right] \log_{10} Q_9 \]  

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 NH\(_3\) emission (CAE) across all soils, temperatures, and moisture regimes was 5787, 7461, 3010 g ha\(^{-1}\) for (NH\(_4\))\(_2\)SO\(_4\), urea, and NH\(_4\)NO\(_3\), respectively. This indicated that the average CAE from NH\(_4\)NO\(_3\) was about half that of either (NH\(_4\))\(_2\)SO\(_4\) or urea because the amount of NH\(_4^+\) in a mole of NH\(_4\)NO\(_3\) is about 50% of that in a mole of either (NH\(_4\))\(_2\)SO\(_4\) 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\(^{-1}\) from 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% 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°C and 11°C, respectively. This disparity in NH\(_3\) emission rates is primarily 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 NH\(_4^+\) source applied to the soil surface and for the transfer of dissolved NH\(_4^+\) 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 KNO\(_3\) (Table 2).
**Table 2. Cumulative NH₃ 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).**

<table>
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<tr>
<th>Soil</th>
<th>Cumulative NH₃ emission</th>
<th>20% FC</th>
<th>80% FC</th>
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<tr>
<td></td>
<td>29°C</td>
<td>20°C</td>
<td>11°C</td>
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<td>(NH₄)₂SO₄</td>
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</table>

- 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.
of NH₃ emission, however, was not evident at 11 to 20°C across all soils evaluated in this study.

The NH₃ emission from urea involves different reactions than those for NH₃ emission from (NH₄)₂SO₄ or NH₄NO₃. At 20% FC, all of the AQ₉ values for NH₃ 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 AQ₉ values for NH₃ emission from urea applied to the BMS and WSL soils increased to almost 3 on Day 28. In contrast, the AQ₉ values for the KGL and QFS soils steadily declined and became zero or negative after Day 14. At 80% FC and 11 to 20°C, the AQ₉ 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 AQ₉ 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 NH₃ emission decreased with time because an AQ₉ 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 AQ₉ for NH₃ emission from urea applied to different soils were much smaller than those from either (NH₄)₂SO₄ or NH₄NO₃ (Fig. 6–8) due to the lag time required for transformation of urea into the NH₄⁺ 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 NH₃ volatilization from urea.

**DISCUSSION**

**The Arrhenius Activation Energy of Ammonia Volatilization**

The \( E_a \) values for different soils amended with either (NH₄)₂SO₄ or NH₄NO₃ 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 NH₄NO₃ at 24.5°C was negative because the NH₃ 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 NH₄⁺ desorption potential of the soils. At 24.5°C, the \( E_a \) value for the WSL soil with either an (NH₄)₂SO₄ or NH₄NO₃ 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 NH₄⁺ ions in the soil solution for a longer period of time, which favors decreased NH₃ volatilization. Dynamic equilibrium between NH₄⁺ and NH₃ in the soil solution is described as follows:

\[
\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + H^+ \quad [7]
\]

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

where \( K_a \) is the acid dissociation constant of NH₄⁺. Furthermore, Eq. [8] may be written in logarithmic form:

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

Since \( -\log_{10}[H^+] \) is the pH and \( -\log_{10} K_a \) is the \( pK_a \), the following equation describes the relationship between NH₃ and NH₄⁺ at a given pH:

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

Therefore, the NH₃ to NH₄⁺ ratio was 1:617 (\( pK_a = 9.25 \)) 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 NH₄⁺ (i.e., NH₄⁺) is really adsorbed by soil particles via strong bonds. Desorption of NH₄⁺ adsorbed via chemisorption requires much more energy than that adsorbed via physical adsorption.

The $E_a$ for desorption of NH₄⁺ 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 NH₄⁺ adsorption. In contrast, the WSL soil with low electrical conductivity provides a greater amount of surface functional groups available for NH₄⁺ adsorption. This may explain, in part, the greater energy required for NH₃ emission from applied NH₄⁺--N from the WSL soil than from the BMS. In soils where a large proportion of ions other than NH₄⁺ 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 NH₄⁺ is maintained in the soil solution due to a low proportion of NH₄⁺ being adsorbed by the soil particles. Hence, the free NH₄⁺ ions are readily volatilized compared with NH₄⁺ ions that are adsorbed.

At 11 to 20°C, the $E_a$ was greater for NH₄NO₃ than for (NH₄)₂SO₄ in all four soils (Fig. 9). This may suggest that the NH₄⁺ ions from NH₄NO₃ were adsorbed by a force stronger than that required for the absorption of NH₄⁺ ions derived from (NH₄)₂SO₄ because NH₄NO₃ yields only half as many NH₄⁺ ions as (NH₄)₂SO₄ and this half quantity of NH₄⁺ ions derived from NH₄NO₃ may be sufficient to just occupy the functional groups via chemisorption. The results of this study suggest that application of NH₄⁺ at high rates would result in high NH₃ emissions due to the presence of NH₄⁺ ions far exceeding the adsorption capacity of the soil, especially those functional groups via chemisorption.

### Isothermal Point of Ammonia Volatilization

Using the AQ₉ curves, we can estimate the duration required for similar amounts of NH₃ emission from different N fertilizer sources. The point of intersection of AQ₉ curves with the x axis is called the isothermal point of ammonia volatilization (IPAV). Based on this criterion, the AQ₉ 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 AQ₉ values were in a range from 1.0 to -1.0, were not sensitive to temperature
increases, i.e., their curves just meandered about the x axis when the soil was incubated at different temperatures. The AQ9 curves of the BMS, KGL, and QFS soils belong to this group. Those with or without an IPAV and with AQ9 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 (NH4)2SO4 occurred after Day 7 in the 20 to 29°C temperature range and 80% FC (Fig. 6); however, the AQ9 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 NH3 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 NH3 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.

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 NH3 emission rates were basically negative, even though they seemed slightly positive at the beginning. Thus the initially higher rates of NH3 emission might not be due to temperature but to the abundance of NH4+ 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 NH4+ adsorption and, hence, the NH3 emission rates differed greatly. This may provide important insight into N fertilizer management aimed at reduction of N2O emissions (Sutton et al., 1998). About 4% of the globally emitted NH3 can be oxidized by OH radicals and NO2 (Finlayson-Pitts and Pitts, 2000). A fraction of the oxidized NH3 is transformed to N2O and this can constitute 5% of the global N2O emission (Ferm, 1998).

Both Ea and IPAV suggested that the NH3 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 NH3 volatilization in the BMS, KGL, and QFS soils. Further research is needed to apply these new concepts of Ea or IPAV in relation to NH3 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 Q9 and AQ9 terms for NH3 emission were introduced to describe the relationship between the rate of NH3 emission and changes in temperature. Unlike the Q9, which represents only the qualitative relationship, the AQ9 describes the qualitative and quantitative relationship between NH3 emission and temperature. The Ea is the Arrhenius activation energy for desorption of the NH4+ ion from soil particles. This study demonstrated that, among the four soils evaluated, the temperature dependence of NH3 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 NH4NO3 or (NH4)2SO4 amended to the
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 (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ 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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REFERENCES