

# Moisture Quotients for Ammonia Volatilization from Four Soils in Potato Production Regions

G. D. Liu · Y. C. Li · A. K. Alva

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**Abstract** Ammonia ( $\text{NH}_3$ ) emission from nitrogen (N) fertilizers used in agriculture decreases N uptake by the crop and negatively impacts air quality. In order to better understand the factors influencing  $\text{NH}_3$  emission from agriculture, this research was conducted with four major soils used for potato production: Biscayne Marl Soil (BMS, pH 7.27), and Krome Gravelly Loam (KGL, pH 7.69) from Florida; and Quincy Fine Sand (QFS, pH 6.65), and Warden Silt Loam (WSL, pH 6.46) from Washington. Potassium nitrate ( $\text{KNO}_3$ ), ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) or urea ( $(\text{NH}_2)_2\text{CO}$ ) sources were evaluated for ammonia volatilization at  $75 \text{ kg N ha}^{-1}$  rate. The soil water regime was maintained at either 20 or 80% of field capacity (FC), and incubated at 11, 20 or  $29^\circ\text{C}$ . Results indicated that  $\text{NH}_3$  volatilization rate at 20% FC was 2 to 3-fold greater than that at 80% FC. The cumulative volatilization loss over 28 days ranged

from 0.21% of N applied as  $\text{NH}_4\text{NO}_3$  to 25.7% as  $(\text{NH}_4)_2\text{SO}_4$ . Results of this study demonstrate that  $\text{NH}_3$  volatilization was accelerated at the low soil water regime. Moisture quotient (Q) is defined as a ratio of  $\text{NH}_3$  emission rate at 20% FC to that at 80% FC both at the same temperature. The peak Q values of  $\text{NH}_3$  volatilization were up to 20.8 for the BMS soil at  $20^\circ\text{C}$ , 112.9 for the KGL soil at  $29^\circ\text{C}$ , 19.0 for the QFS soil at  $20^\circ\text{C}$ , and 74.1 for the WSL soil at  $29^\circ\text{C}$ , respectively. Thus, maintaining a suitable soil water regime is important to minimize N-loss via  $\text{NH}_3$  volatilization and to improve N uptake efficiency and air quality.

**Keywords** Ammonia emission · Soils from Florida and Washington · Fertilizers · Soil water regimes · Nitrogen management for potatoes

## 1 Introduction

Ammonia ( $\text{NH}_3$ ) emission from agriculture including livestock wastes has been recognized since the early nineteenth century (Boussingault 1851; Bussink and Oenema 1998; Sprengel 1839). Ammonia volatilization from N fertilizers used for agricultural production reduces utilization efficiency of applied nitrogen (N) fertilizers. The direct annual world-wide economic loss due to  $\text{NH}_3$  volatilization from chemical N fertilizers applied to farmlands is US\$11.6 billion

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(FAO 2001). Ammonia volatilization also causes serious climatic and environmental problems (Gay and Knowlton 2005; NRC 2003). Ammonia emission occurs from livestock manure as well. However, contribution from this source is rather insignificant as compared to the global ammonia emission from chemical N fertilizers. Therefore, research interests on ammonia emission from animal manures were rather subdued in the early 1950s. (Bussink and Oenema 1998). However, interest in this area of research increased with the realization of negative environmental impact of gaseous N emission on air quality and their contribution to greenhouse gases (Aneja et al. 2006; Buijsman et al. 1987; Fangmeier et al. 1994; Gay and Knowlton 2005; Kirchmann et al. 1998; Van Breeman et al. 1982). Ammonia emission from agricultural sources contributes to a significant portion of total  $\text{NH}_3$  emission (Ferm 1998; Schlesinger and Hartley 1992). In the Western Europe 92% of all  $\text{NH}_3$  emission was traced to agricultural origins (Kirchmann et al. 1998). Consequently, reduction in  $\text{NH}_3$  emission from agricultural production practices should increase the utilization efficiency of applied N fertilizers and improve air quality (Aneja et al. 2006; Buijsman et al. 1987; Fangmeier et al. 1994; Gay and Knowlton 2005; Kirchmann et al. 1998; Van Breeman et al. 1982).

Volatilized  $\text{NH}_3$  is the only natural alkaline gas in the earth's atmosphere (Asman et al. 1982; Schlesinger and Hartley 1992).  $\text{NH}_3$  has a relatively short residence time in the atmosphere, about 10 days, due to its rapid conversion to nitrous oxide ( $\text{N}_2\text{O}$ ) (Dentener and Crutzen 1994) and to ammonium ( $\text{NH}_4^+$ ), and the deposition of  $\text{NH}_3$  onto soil and water surfaces (Aneja et al. 1998; Fowler et al. 1997). There is an annual flux of about  $75 \times 10^6$  MT (metric tones) of N derived from the global sources of  $\text{NH}_3$  emitted into the atmosphere (Schlesinger and Hartley 1992). Indeed,  $\text{NH}_3$  is the third most abundant N gas (after  $\text{N}_2$  and  $\text{N}_2\text{O}$ ) in the atmosphere.

The emitted  $\text{NH}_3$  can partially be deposited *in situ* (within ca 50 km from the source) or *ex situ* (ca 400 km from the source) by either dry deposition or wet deposition (Duce et al. 1991; Ferm 1998; Schlesinger and Hartley 1992; Warneck 1999). Schlesinger and Hartley (1992) estimated that 76% of emitted  $\text{NH}_3$  ( $57 \times 10^6$  MT N/yr) was deposited onto water or soil surfaces. This deposited  $\text{NH}_3$  causes environmental problems such as soil and water body acidification,

eutrophication and forest dieback (Fangmeier et al. 1994; Van Breeman et al. 1982). Pearl (1991, 1995) reported signs of enhanced eutrophication in several estuarine and coastal ecosystems impacted by atmospheric N deposition.

In addition to soil and water body pollution, the emitted  $\text{NH}_3$  exacerbates global climate change. Dentener and Crutzen (1994) estimated that 4% ( $3 \times 10^6$  MT N/yr) of the globally emitted  $\text{NH}_3$  can be oxidized by OH radicals and  $\text{NO}_2$  (Finlayson-Pitts and Pitts 2000), mainly in the tropics. A fraction of the oxidized  $\text{NH}_3$  is transformed to  $\text{N}_2\text{O}$  and this can constitute 5% of the global  $\text{N}_2\text{O}$  emission (Ferm 1998).  $\text{N}_2\text{O}$  is a potent greenhouse gas and approximately 310-fold more powerful than  $\text{CO}_2$  in trapping heat in the atmosphere (Finlayson-Pitts and Pitts 2000; IPCC 1996).

The remainder of the emitted  $\text{NH}_3$  reacts with acid gases such as  $\text{SO}_2$  generated from fossil fuel combustion; and these reactions provide a major portion of the ambient fine particulate matter that is called PM<sub>2.5</sub> (the fraction of aerosol particles with an aerodynamic diameter less than 2.5  $\mu$ ) (Finlayson-Pitts and Pitts 1986). PM<sub>2.5</sub> particles are harmful to human health (Dockery et al. 1993; Kelsall et al. 1997; Marcezzan et al. 2001; Pagano et al. 1998; Schwartz et al. 1996) because they can be inhaled and can penetrate into the gas-exchange region of the lung (Brunekreef and Holgate 2002). Therefore, PM<sub>2.5</sub> particles cause numerous health problems including asthma, bronchitis, and acute and chronic respiratory symptoms such as shortness of breath and painful breathing, and premature deaths.

Although  $\text{NH}_3$  loss from agriculture has been recognized for almost two centuries (Bussink and Oenema 1998), the control of  $\text{NH}_3$  emission from anthropogenic activities is still uncertain. Fenn and Hossner (1985) reported that the variability in soil water content is probably the major factor affecting  $\text{NH}_3$  loss from surface applied N fertilizers. However, there are many conflicting reports on the effects of soil moisture on  $\text{NH}_3$  volatilization. Fox and Hoffman (1981) reported that less than 10%  $\text{NH}_3$  loss occurred if 10 mm rainfall fell within 3 days after application of urea but the  $\text{NH}_3$  loss was greater than 30% if there was no rainfall within 6 days after application. Their results showed that high soil moisture reduced  $\text{NH}_3$  loss via volatilization. However, Sommer et al. (2004) found that high moisture content of the surface layer

of soil was one of the most important environmental factors causing high rates of  $\text{NH}_3$  volatilization from applied N-fertilizers. Previously, Fenn and Hossner had discovered that a soil surface with low moisture content reduced  $\text{NH}_3$  loss from surface applied urea and inorganic N fertilizers in the field. Vlek and Carter (1983) showed that urea hydrolysis at the permanent wilting point (PWP) was relatively high but decreased rapidly with further soil drying because soil urease requires adequate surface water to facilitate substantial rates of urea hydrolysis (Fox and Hoffman 1981). Soil urease may not be able to maintain its activity to hydrolyze urea because available water is limited, as when the water potential is lower than that at the PWP. These conflicting results can be attributed mainly to different experimental conditions or research methods. They may also result from the failure to model the effects of moisture on  $\text{NH}_3$  emission because the effects of moisture differ with time, soil type, fertilizer species, temperature, and the like. Currently, the basic factor, that indicates the effects of soil moisture on  $\text{NH}_3$  volatilization, is the percentage change between soil water regimes (Fox and Hoffman 1981). Percentage is a useful indicator when a small number of different soil moisture levels are analyzed but not when a large body of data must be done. Actually, the current references focus on a single comparison between various soil-moistures (Fenn and Miyamoto 1981; Fox and Hoffman 1981) because it is not convenient to monitor the dynamic effects of changing moisture levels on  $\text{NH}_3$  emission in a period of time without the benefit of a scientific concept or model. We propose that the “moisture quotient” is a potentially useful concept to describe the effects of soil moisture levels on  $\text{NH}_3$  emission.

The concept of moisture quotient was introduced by Emberger (1955). This concept and the mapping of bioclimatic zones resulted in the zoning of vegetation. Indeed, the moisture quotient continues to be of fundamental value to geographers and climatologists. Additionally, the concept is used in studies to elucidate the mechanisms of control of damage by wood-boring insects, rot fungi, and stain fungi to timbers in buildings (Oliver 1997; Viitanen 1997; Voutilainen 2005). However, no literature reports could be found on the use of the moisture quotient to elucidate the effects of moisture levels on  $\text{NH}_3$  emission rates from different soils subject to varying conditions.

The moisture quotient is defined as the ratio of the  $\text{NH}_3$  volatilization rate at one moisture level to that at a higher moisture level (20 and 80% FC, respectively in this study); both under identical temperature and other environmental conditions. The moisture quotient may be used to assess the dynamic effects of soil moisture level on  $\text{NH}_3$  volatilization.

The objectives of this research were to: (1) present a new concept of the moisture quotient to describe the effects of soil water content on  $\text{NH}_3$  volatilization losses from different N sources; (2) model the effects of soil moisture on  $\text{NH}_3$  volatilization using the concept of the moisture quotient; and (3) quantify the moisture quotients of  $\text{NH}_3$  volatilization from different N sources applied to a variety of soils at several temperatures.

## 2 Materials and Methods

### 2.1 Soils

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). The main rotation on both of the BMS and KGL soils is potato–sweet corn. Fertilizer application rates are 220 kg N ha<sup>-1</sup> for potato production and 220 kg N ha<sup>-1</sup> for sweet corn under center pivot irrigation system. Quincy Fine Sand (QFS, Mixed, mesic Xeric Torripsamments) and Warden Silt Loam (WSL, Coarse-silty, mixed, mesic, Xerollic Camborthids, dark grayish-brown soil) occur in the Columbia Basin potato production region in south central Washington (Liu et al. 2007). The typical rotation on both soils has been corn–wheat–potato under center pivot irrigation system. Fertilizer history for potato has been: 112 kg ha<sup>-1</sup> N as urea broadcast pre-planting application, and 224 kg N ha<sup>-1</sup> as in-season fertigation (using urea ammonium nitrate solution, through pivot) in five equally split applications at 2 weeks interval starting 3 weeks after seedling emergence. For corn and wheat: 224 kg N ha<sup>-1</sup> as urea is applied during cultivation. No in-season N application is followed. All four soils have been used extensively for crop production but have different acidities. The

**Table 1** Characteristics of the soils tested from Florida and Washington

Soil	Source location	pH	EC <sup>c</sup> (μS/cm)	SHC <sup>f</sup> cm/hr	Total P (mg/kg)	Total N (%)	OM <sup>g</sup> (%)	Particle size (%)		
								Clay	Silt	Sand
BMS <sup>a</sup>	Florida	7.27	457.0	9.2	4,240.4	0.29	1.49	17.48	73.20	9.31
KGL <sup>b</sup>	Florida	7.69	131.0	317.0	1,021.3	0.13	1.79	7.97	34.48	57.55
QFS <sup>c</sup>	Washington	6.65	49.0	na <sup>h</sup>	1,083.7	0.04	0.41	1.88	11.24	86.88
WSL <sup>d</sup>	Washington	6.46	93.0	na	3,377.6	0.07	0.67	2.46	40.49	57.05

<sup>a</sup> Biscayne Marl Soil, <sup>b</sup> Krome Gravelly Loam, <sup>c</sup> Quincy Fine Sand, <sup>d</sup> Warden Silt Loam. <sup>e</sup> Electrical conductivity. <sup>f</sup> Saturated hydraulic conductivity, source: Muñoz-Carpena et al. 2005. <sup>g</sup> Organic matter. <sup>h</sup> not available.

two from Florida are basic soils with pH 7.27 for the BMS soil and 7.69 for the KGL soil. The two from Washington are acidic soils with pH 6.65 for the QFS soil and the 6.45 for the WSL soil. Some of the properties and fertilizer history of these soils are presented in Tables 1 and 2.

## 2.2 Incubation Temperature

The incubation temperatures chosen for use in this study were based on the mean temperature in the selected production regions during the growing season. In the Columbia Basin production region of Washington, the maximum, average and minimum temperatures for the potato growing season are 29, 20 and 11°C, respectively, based on the daily climatic data for 2000 through 2003. In Florida, the growing season for potato is from October to May. The corresponding maximum, average and minimum temperatures are 26.5, 22.5 and 18.4°C. These temperatures are within the range of those in Washington; hence, 29, 20 and 11°C were used as the incubation temperatures for this investigation.

## 2.3 Soil Moisture Content During Incubation

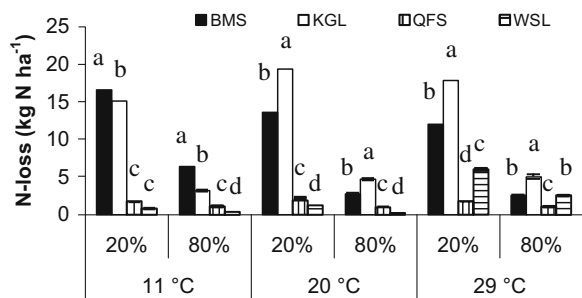
Soil water contents at field capacities of the BMS, KGL, QFS, and WSL soils were measured for all four soils using the classic transient drainage method: A 250 ml plastic cup with 12 1-mm-diameter holes distributed evenly at the bottom was filled with about 200 g of each of the four soils in three replicates (4 soils × 3 replicates = 12 cups). The soil in the cup was flooded over night and allowed to drain until the drainage stopped completely. Gravitational soil water content was determined which represents the field capacity water content for each soil. The incubation of the treated soils was done at 20 and 80% FC soil water contents for the respective soils. After the bottles were set up, each bottle was placed inside a sealed plastic Ziploc storage bag (23 × 30 cm) to avoid any moisture loss.

## 2.4 Ammonia Trapping and Chemical Analysis

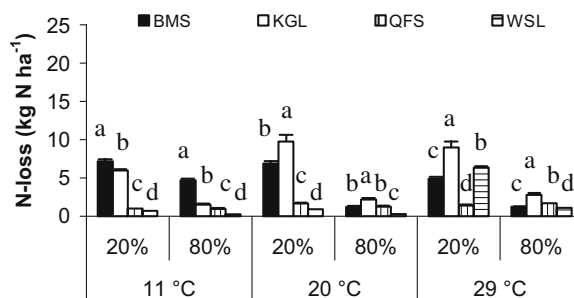
Three hundred grams (dry weight) of each soil was placed in a 500-ml incubation bottle (Liu et al. 2007). The soil-surface area in the bottle was about 60 cm<sup>2</sup>.

**Table 2** The cropping systems and N fertilization (kg ha<sup>-1</sup>) in the soils in the study

			Soil site rotation	BMS Florida potato–sweet corn	KGL Florida potato–sweet corn	QFS Washington corn–wheat–potato	WSL Washington corn–wheat–potato
Fertilization	N	Corn	Pre-planting	70	70	224	224
			In-season	150	150	0	0
	Wheat	Pre-planting	–	–	224	224	
		In-season	–	–	0	0	
	Potato	Pre-planting	70	70	112	112	
		In-season	150	150	224	224	

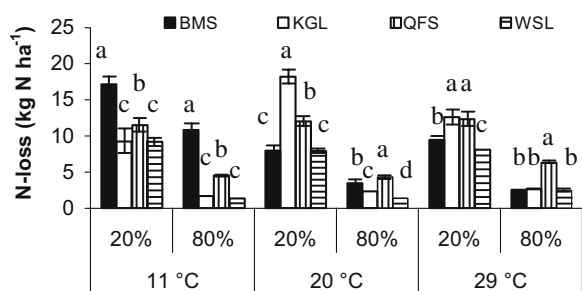


**Fig. 1** Cumulative N-loss over 28 d via ammonia emission from four soils amended with  $(\text{NH}_4)_2\text{SO}_4$  at either 20 or 80% field capacity (FC) and 11, 20 or 29°C incubation temperatures. *BMS*: Biscayne Marl Soil; *KGL*: Krome Gravelly Loam; *QFS*: Quincy Fine Sand; *WSL*: Warden Silt Loam. Vertical bars not followed by the same letter are significantly different at  $P \leq 0.05$  by DMRT at the same temperature and soil water regime



**Fig. 3** Cumulative N-loss over 28 d via ammonia emission from four soils amended with  $\text{NH}_4\text{NO}_3$  at either 20 or 80% FC and 11, 20 or 29°C incubation temperatures. *BMS*: Biscayne Marl Soil; *KGL*: Krome Gravelly Loam; *QFS*: Quincy Fine Sand; *WSL*: Warden Silt Loam. Vertical bars not followed by the same letter are significantly different at  $P \leq 0.05$  by DMRT at the same temperature and soil water regime

The soil water content was adjusted to either 20 or 80% FC. The water content at FC for the four soils evaluated in this study was (v/m based on oven dry soils):  $604.5 \pm 11.2$ ,  $323.4 \pm 6.7$ ,  $247.4 \pm 2.7$ , and  $326.1 \pm 2.8 \text{ ml kg}^{-1}$  for the *BMS*, *KGL*, *QFS*, and *WSL* soils, respectively. One ml of  $45 \text{ mg N ml}^{-1}$  solution [as one of the following: either ammonium sulfate- $(\text{NH}_4)_2\text{SO}_4$ , or urea- $(\text{NH}_2)_2\text{CO}$ , ammonium nitrate- $\text{NH}_4\text{NO}_3$ , or potassium nitrate- $\text{KNO}_3$ ] was uniformly applied on the soil surface with a micropipette. The amount of N applied was  $45 \text{ mg N}$  per bottle, equivalent to  $75 \text{ kg N ha}^{-1}$  based on surface area of the soil in the bottle. A treatment with only deionized water was included as a control. Thus, there were 4 soils  $\times$  5 N sources (including the control)  $\times$  3 temperatures  $\times$  2 soil water regimes  $\times$  3 replications



**Fig. 2** Cumulative N-loss over 28 d via ammonia emission from four soils amended with urea at either 20 or 80% FC and 11, 20 or 29°C incubation temperatures. *BMS*: Biscayne Marl Soil; *KGL*: Krome Gravelly Loam; *QFS*: Quincy Fine Sand; *WSL*: Warden Silt Loam. Vertical bars not followed by the same letter are significantly different at  $P \leq 0.05$  by DMRT at the same temperature and soil water regime

which required 360 total incubation bottles. Each incubation bottle was placed in a sealed plastic Ziploc storage bag ( $23 \times 30 \text{ cm}$ ) and placed in an incubator at 11, 20 or 29°C, as appropriate. A sponge spiked with the trapping solution was inserted into the mouth of the bottle to trap the volatilized  $\text{NH}_3$ . Each sponge (about 5 cm in diameter) was cut from Yellow Flower Sponge material (Arrow Plastic Manufacturing Company, Elk Grove Village, IL). Each cut sponge was spiked with 0.8 ml of trapping solution consisting of 35 ml of concentrated phosphoric acid, 250 ml of 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 days and a new sponge (with the trapping solution) was inserted into the mouth of the bottle to trap  $\text{NH}_3$  for each subsequent incubation period. The ammonia in sponges was extracted with 25 ml of 1 M KCl and measured using an Auto Analyzer III (Bran+Luebbe GmbH, Werkstrasse, Norderstedt, Germany, <http://www.bran-luebbe.de>) according to EPA Method 350.1 (EPA 1993).

### 2.5 Moisture Quotient ( $Q$ ) and Active Moisture Quotient ( $AQ$ ) of Ammonia Volatilizations

The moisture quotient ( $Q$ ) of  $\text{NH}_3$  volatilization is the ratio of  $\text{NH}_3$  volatilization rates at two different soil moisture levels both under the same temperature and soil conditions.  $Q$  is defined in this research as follows:

$$Q = \frac{R_2}{R_1} \left( \left| \frac{FC_2 - FC_1}{0.60} \right| \right) \tag{1}$$

**Table 3** Soil water content (ml 100<sup>-1</sup> g) of the four soils used in this study over a range of field capacity (FC) regimes

	100% FC TW <sup>a</sup>	BW <sup>b</sup>	80%FC TW	AW <sup>c</sup>	20%FC TW	AW
BMS <sup>d</sup>	60.5±1.1 <sup>h</sup>	1.6±0.0	48.4	46.7	12.1	10.5
KGL <sup>e</sup>	32.3±0.7	3.0±0.1	25.9	22.8	6.5	3.4
QFS <sup>f</sup>	24.7±0.3	0.8±0.0	19.8	19.0	5.0	4.1
WSL <sup>g</sup>	32.6±0.3	1.7±0.0	26.1	24.4	6.5	4.9

<sup>a</sup>Total water volume. <sup>b</sup>Bound water volume which is the difference between wind-dried and oven-dried (105°C for 6 h) soil, <sup>c</sup>Available water volume, <sup>d</sup>Biscayne Marl Soil, <sup>e</sup>Krome Gravelly Loam, <sup>f</sup>Quincy Fine Sand, <sup>g</sup>Warden Silt Loam, <sup>h</sup>The values are Mean ± STD.

where  $Q$  is the moisture quotient of the rates of NH<sub>3</sub> volatilization.  $R_1$  and  $R_2$  are the rates of NH<sub>3</sub> volatilization at either 80% ( $FC_1$ ) or 20% ( $FC_2$ ) under the same temperature. Therefore,  $FC_1 - FC_2 = 60\%$ , and  $(FC_1 - FC_2)/0.60 = 100\%$ .

$Q$  is a scalar quantitative measure of the change in NH<sub>3</sub> volatilization rate; but  $Q$  is a scalar quantity, which does not indicate the direction (increase or decrease) of the change in the NH<sub>3</sub> volatilization rate between different soil moisture levels. In order to describe both quantitative and qualitative changes of NH<sub>3</sub> volatilization rate, active moisture quotient ( $AQ$ ) is used and defined as follows.

$$AQ = \frac{R_2 - R_1}{R_1} \left( \left| \frac{FC_2 - FC_1}{0.60} \right| \right) \quad (2)$$

where  $AQ$  is the active moisture quotient of the rates of NH<sub>3</sub> volatilization, and the other symbols are the same as those in Eq 1.

## 2.6 Statistical Analysis

The Statistical Analysis System (SAS) package version 9.1, (2003, SAS Institute, Inc., Cary, NC), was used to perform the statistical analyses. The data were tested by Duncan's Multiple Range Test (DMRT) with a statistical significance of  $P \leq 0.05$ .

## 3 Results and Discussions

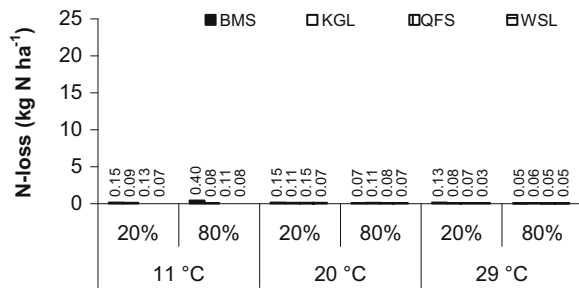
### 3.1 Differences in Cumulative N-loss Between Two Soil Water Regimes

There were significant differences in cumulative NH<sub>3</sub> emission between 20 and 80% FC over the 28 d incubation period across all N sources and all incubation temperatures (Figs. 1, 2 and 3). Cumulative N-losses across the four soils at 20% FC were

**Table 4** Summary of ANOVA test for factors influencing NH<sub>3</sub> emission

Source	DF	Anova SS	Mean square	F value	Pr > F
Moisture	1	1.95E+09	1.95E+09	978.13	<.0001
Fertilizer	4	6.09E+09	1.52E+09	763.7	<.0001
Soil	3	1.28E+09	4.27E+08	214.35	<.0001
Time	4	1.66E+09	4.14E+08	207.86	<.0001
Temperature	2	5.10E+07	2.55E+07	12.81	<.0001
Replicate	2	1.19E+04	5.94E+03	0.00	0.9970
Fertilizer × Moisture	4	1.63E+09	4.07E+08	204.24	<.0001
Soil × Fertilizer	12	2.80E+09	2.33E+08	117.03	<.0001
Soil × Moisture	3	4.94E+08	1.65E+08	82.62	<.0001
Time × Moisture	4	4.82E+08	1.20E+08	60.41	<.0001
Time × Fertilizer	16	1.65E+09	1.03E+08	51.78	<.0001
Soil × Temperature	6	2.67E+08	4.45E+07	22.33	<.0001
Time × Soil	12	2.47E+08	2.06E+07	10.33	<.0001
Fertilizer × Temperature	8	5.07E+07	6.34E+06	3.18	0.0014
Temperature × Moisture	2	1.42E+07	7.09E+06	3.56	0.0286
Time × Temperature	8	2.36E+07	2.95E+06	1.48	0.1589





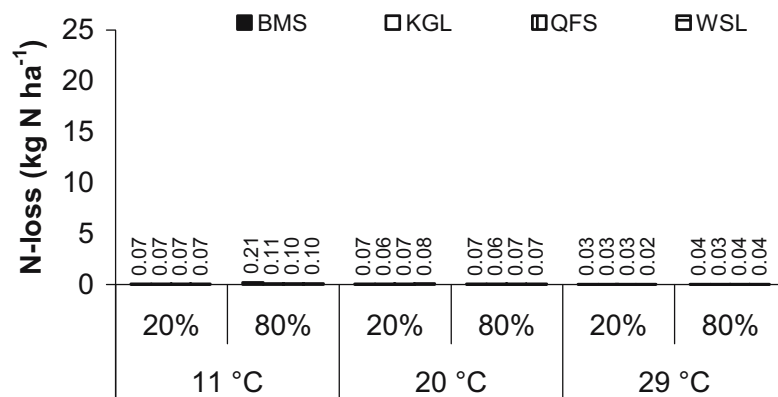
**Fig. 4** Cumulative N-loss over 28 d via ammonia emission from four soils amended with KNO<sub>3</sub> at either 20 or 80% FC and 11, 20 or 29°C incubation temperatures. *BMS*: Biscayne Marl Soil; *KGL*: Krome Gravelly Loam; *QFS*: Quincy Fine Sand; *WSL*: Warden Silt Loam. The columns are not appearing because the cumulative N-losses were too small. To show the amount of the N-losses, the values are presented on the figure

3.3-, 4.1- and 3.5-fold greater than those at 80% FC for (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, urea, NH<sub>4</sub>NO<sub>3</sub>, respectively. Ammonia volatilization loss was 19.3 kg N ha<sup>-1</sup> for the KGL soil amended with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> incubated at 20°C and 20% FC. The least N loss from the applied fertilizers with instant or convertible NH<sub>4</sub>-N source was 0.2 kg N ha<sup>-1</sup> for the WSL soil amended with NH<sub>4</sub>NO<sub>3</sub> incubated at 20°C and 80% FC.

Soil water can be simply categorized as free (available) water, and bound (unavailable) water. Water can be bound to the soil matrix by adhesive forces, cohesive forces and osmotic forces (Hilhorst et al. 2001; Koorevaar et al. 1983). Unlike unbound water, bound water loses its energy and is able to exert little influence on the soil processes because its water molecules are absorbed to the surface of

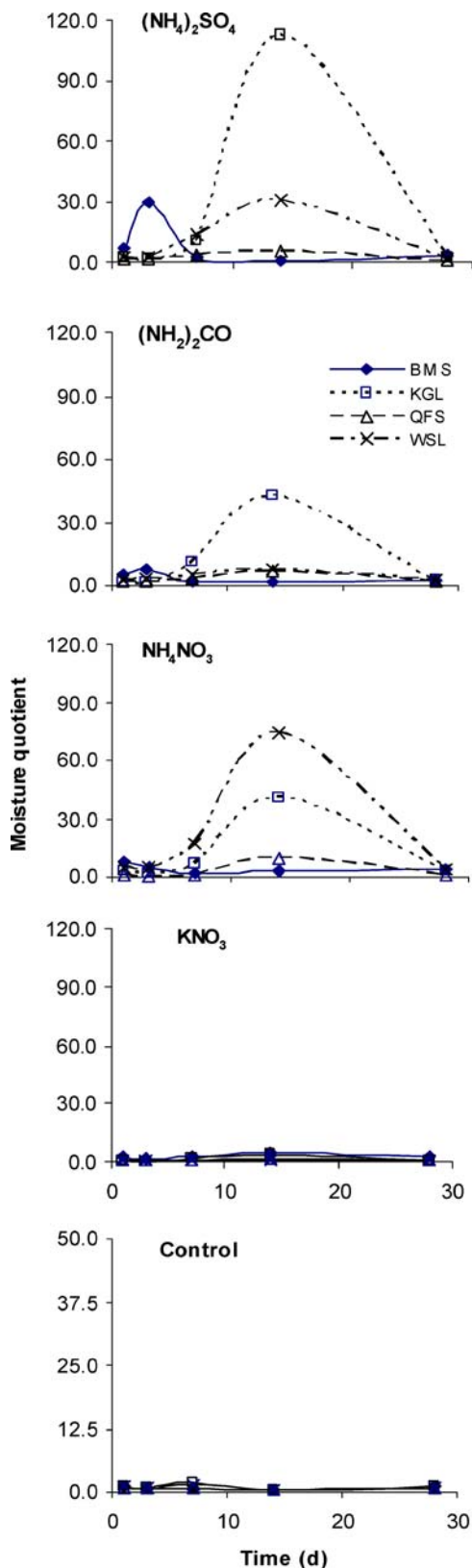
particles and the dipoles are immobilized (Jackson and Schmutge 1989; Njoku and Entekhabi 1996). For example, bound water doesn't act as a solvent, which is needed to transport ammonium (NH<sub>4</sub><sup>+</sup>) in the soil. Among the four soils, KGL contained the least amount of free water at 20% FC (Table 3). Additionally, saturated hydraulic conductivity of the KGL soil was 34-fold greater than that of the BMS soil (Table 1, Muñoz-Carpena et al. 2005). This shows that the water-holding ability of the KGL soil was very poor. The results for the four soils showed that the lower the soil moisture content, the higher was the amount of NH<sub>3</sub> volatilization (Figs. 1, 2 and 3 and Table 3). Therefore, N fertilizer management and water management should be integrated to minimize NH<sub>3</sub> emission. Furthermore, adoption of crop genotypes that are water efficient and thorough weed control may mitigate soil water stress and decrease NH<sub>3</sub> emission to the atmosphere. Ammonia emissions from the BMS and KGL soils were greater than that from the QFS and WSL soils. This could be, in part, due to the greater pH of the former as compared to that of the latter soils (Table 1). The pH for the KGL soil was the highest among the four soils evaluated in this study, which recorded the highest NH<sub>3</sub> emission rate among the four soils (Liu et al. 2007).

In limited water-supply situations, it is critical to maintain adequate soil water content during the period immediately following the application of N fertilizers. Likewise, N fertilizer application should be scheduled when the soil contains adequate soil water content. The N-losses from the four soils in the



**Fig. 5** Cumulative N-loss over 28 d via ammonia emission from four soils amended with nothing (control) at either 20 or 80% FC and 11, 20 or 29°C incubation temperatures. *BMS*: Biscayne Marl Soil; *KGL*: Krome Gravelly Loam; *QFS*: Quincy

Fine Sand; *WSL*: Warden Silt Loam. The columns are not appearing because the cumulative N-losses were too small. To show the amount of the N-losses, the values are presented on the figure



control, or KNO<sub>3</sub> amended treatments were negligible. Thus, the following discussion mainly focuses on the NH<sub>3</sub> emission from either (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, urea, NH<sub>4</sub>NO<sub>3</sub>.

ANOVA test shows there were significant interactions between N source × moisture, soil × N source, soil × moisture, time × moisture, time × N source, soil × temperature, time × soil, N source × temperature, and temperature × moisture (Table 4). Particularly, the interactions between moisture and each of the other factors were always highly significant. This further indicates that the importance of adequate soil water management following N fertilization to minimize gaseous N losses.

However, there was little difference when the soils without fertilizer (control) or with fertilizers without any instant or convertible ammonia such as potassium nitrate (Figs. 4 and 5).

### 3.2 Differences in Moisture Quotients of NH<sub>3</sub> Emission Rates

The moisture quotients ( $Q$ ) of NH<sub>3</sub> volatilization rates were associated closely with temperature and soil type (Figs. 6, 7 and 8). The  $Q$  values were dynamic, changing with time because the available NH<sub>3</sub> level decreased with time. At 29°C,  $Q$  increased to a maximum of 112.9 for the KGL soil amended with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (Fig. 6). However at 20°C,  $Q$  increased to a maximum of only 48.3 for the KGL soil amended with urea (Fig. 7). At 11°C,  $Q$  increased to a maximum of 19.3 for the WSL soil amended with NH<sub>3</sub>NO<sub>3</sub> (Fig. 8). All the  $Q$  values for the four soils showed significant differences in the NH<sub>3</sub> emission rates under two soil water regimes. This indicated the NH<sub>3</sub> emission rates under 20% FC significantly higher than those under 80% FC. In the dry soil, the transport of NH<sub>4</sub><sup>+</sup> ions from the soil surface down to deep soil horizon was restricted, hence lead to increased losses as NH<sub>3</sub> emission.

At 29°C, the  $Q$  values for the soils showed a single peak response curve with the peak on day 14 with the exception of the BMS soil in which NH<sub>3</sub> emission peaked on Day 3 for both (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and urea but

◀ **Fig. 6** The moisture quotient ( $Q$ ) at 29°C for the rates of ammonia volatilization from the four soils fertilized with five different N-sources under 20 and 80% FC. BMS: Biscayne Marl Soil; KGL: Krome Gravelly Loam; QFS: Quincy Fine Sand; and WSL: Warden Silt Loam

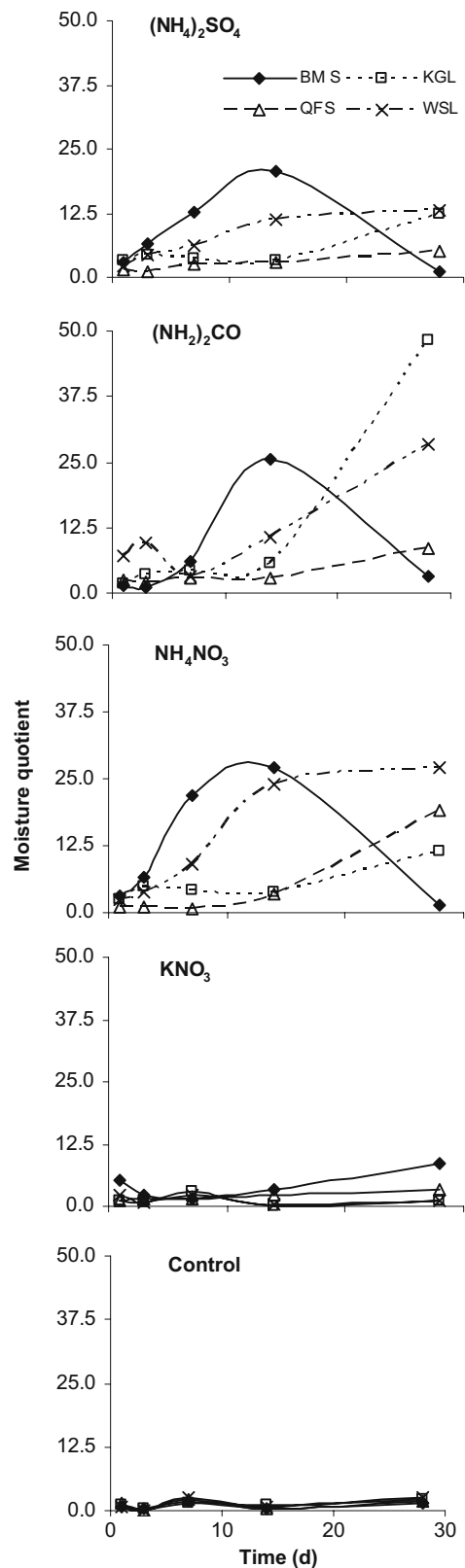


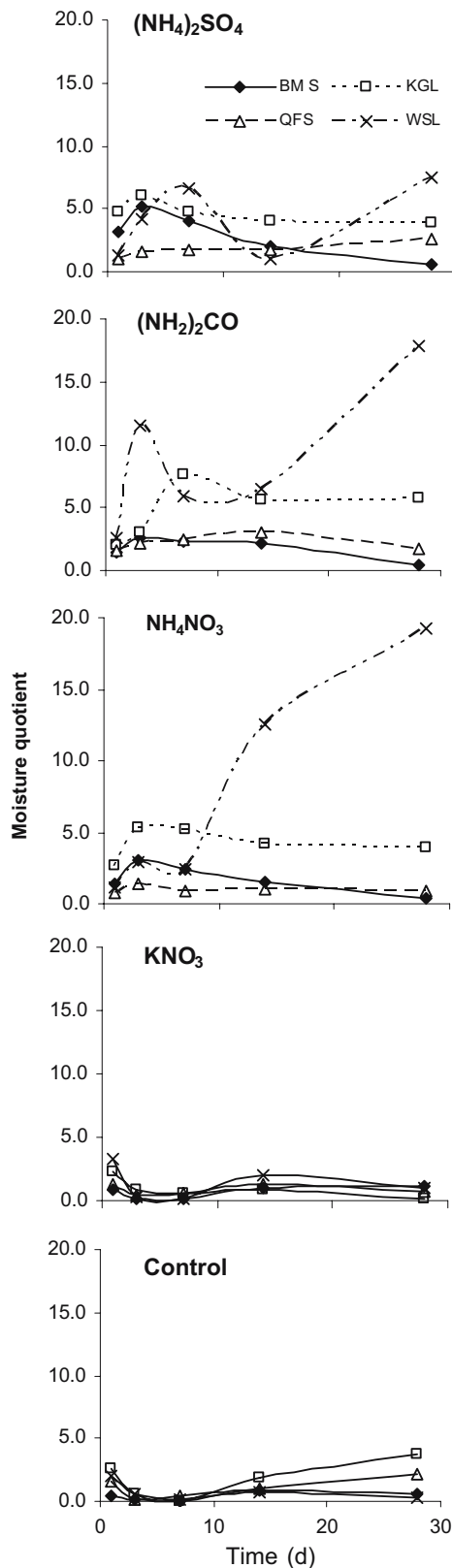
didn't peak for the other treatments (Fig. 6). The deceleration in  $NH_3$  emission could be due to depletion of  $NH_4^+$  sources. At 29°C, the  $Q$  values for the KGL soil were the largest or the second largest among the four soils were using either  $(NH_4)_2SO_4$  or urea. In fact, the maximum  $Q$  values for the KGL soil amended with urea were 5.7 to 6.1-fold greater than those for the BMS, QFS and WSL soils at 29°C. This indicated that the  $NH_3$  emission for the KGL soil was most sensitive to soil water regimes. At 29°C,  $NH_3$  emission from QFS soil was the least responsive to changes in soil water content. With BMS soil at 29°C, the  $Q$  values vs. time showed a rather modest early peak only for  $(NH_4)_2SO_4$  and urea sources (Fig. 6). At 20°C, however, the single peak response of the  $Q$  vs. time was evident only in the BMS soil across all the three N sources with instant or convertible ammonium; while for all other soils, the  $Q$  values increased continuously for the entire duration of this study (Fig. 7).

Vazquez-Rodriguez and Rols (1997) reported that nitrification increased 2.8-fold with every 10°C increment in temperature. The above results may be attributed to a lower rate of nitrification at 20°C than that at 29°C, because  $NH_3$  emission can last longer if the  $NH_4^+$  source is sufficient and a low rate of nitrification would convert only a small amount of  $NH_4^+$  source into  $NO_3^-$ . At 20°C, the effect of lower soil water content on  $NH_3$  emission lasted longer than that at 29°C. Thus the influence of soil water stress on  $NH_3$  emission was weaker at 20°C than at 29°C. Moreover at 11°C, the effects of soil water stress on  $NH_3$  emission from the four soils amended with each of the three N sources were much less evident than those at either 20 or 29°C (Figs. 6, 7 and 8). Among the four soils tested the WSL soil showed the most positive response but the BMS soil showed a negative response 3 days following the incubation. The QFS soil had only small changes in the moisture quotient for the various fertilizers.

The maximum  $Q$  values were 19.3, 48.3 and 112.9 across soils at 11, 20 and 29°C, respectively (Figs. 6, 7 and 8). This suggests an increase in  $NH_3$  emission with increasing water stress. The magnitude of this response

**Fig. 7** The moisture quotient ( $Q$ ) at 20°C for the rates of ammonia volatilization from the four soils fertilized with five different N-sources under 20 and 80% FC. *BMS*: Biscayne Marl Soil; *KGL*: Krome Gravelly Loam; *QFS*: Quincy Fine Sand; and *WSL*: Warden Silt Loam





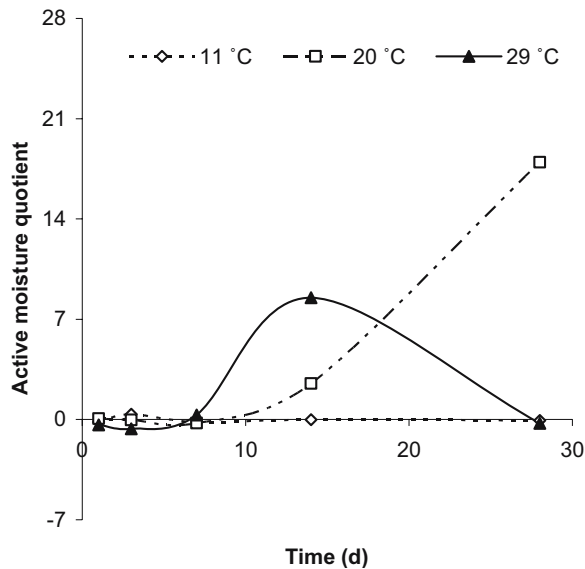
was however variable in different soils. In this experiment, the soil water content was set at 20 and 80% of FC for the respective soils. However, the gravimetric soil water content at a given soil water regime treatment differed substantially across these four soils. The soil water contents at 80% FC treatment were: 48.3, 33.4, 26.0 and 19.8 for the BMS, KGL, WSL and QFS soils, respectively. The corresponding total soil water contents at 20% FC treatment were 12.0, 8.4, 6.7 and 4.8% (Table 3).

There was not much  $Q$  difference in all of the four tested soils amended with  $\text{KNO}_3$  and the control because there was not available ammonium or ammonia source to be emitted (Figs. 6, 7 and 8).

### 3.3 Differences in Active Moisture Quotients of $\text{NH}_3$ Emission Rates

The  $Q$  value is always equal to or greater than 0 and quantitatively indicates the difference in the  $\text{NH}_3$  volatilization rates between two soil moisture levels, but it cannot indicate the direction (positive or negative) of difference because  $Q$  is always  $\geq 0$ . In contrast,  $AQ$  can simultaneously denote both quantity and direction of change because it is either, equal to, less or greater than 0. In this study, the  $AQ$  values were greater than 0 for all of the soils except the BMS and QFS soils amended with  $\text{NH}_4\text{NO}_3$ . This suggests that the low soil water regime greatly enhanced the rate of  $\text{NH}_3$  volatilization. Figure 9 shows that the  $AQ$  values are temperature-dependent, and at  $29^\circ\text{C}$ , a single peak curve is obtained. During the first week, and by Day 28, the  $AQ$  values were negative. The curve intersects the X-axis on about Day 7 and Day 28. This means that at these two points, the  $\text{NH}_3$  volatilization rates are the same at both 20% and 80% FC. These two points can be designated as iso-moisture points (IMP) of  $\text{NH}_3$  volatilization. The  $\text{NH}_3$  volatilization rate at 80% FC was greater than that at 20% FC when the  $AQ$  value was negative and the converse is true when the  $AQ$  value was positive. The reasons for the demonstration of two IMPs may be several. In the days following application of  $\text{NH}_4\text{NO}_3$

◀ **Fig. 8** The moisture quotient ( $Q$ ) at  $11^\circ\text{C}$  for the rates of ammonia volatilization from the four soils fertilized with five different N-sources under 20 and 80% FC. BMS: Biscayne Marl Soil; KGL: Krome Gravelly Loam; QFS: Quincy Fine Sand; and WSL: Warden Silt Loam

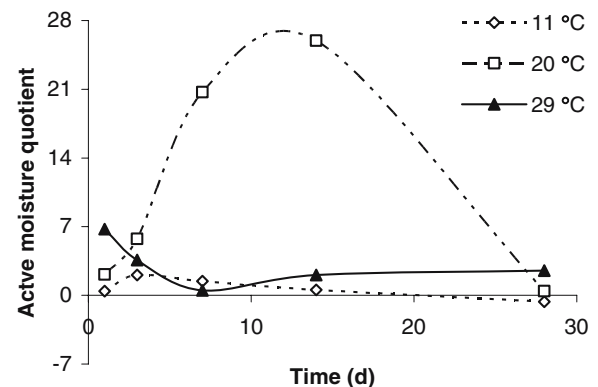


**Fig. 9** The active moisture quotient ( $AQ$ ) for the rates of ammonia volatilization from the QFS soil amended with  $\text{NH}_4\text{NO}_3$  at 11, 20, or 29°C

to the QFS soil,  $\text{NH}_3$  volatilization progressed rapidly under both soil water regimes but at slightly greater rate at 80% FC than that at 20%. This resulted in a negative  $AQ$  values. Subsequently, as the  $\text{NH}_4^+$  ions from  $\text{NH}_4\text{NO}_3$  at 80% FC were transported into deeper soil and adsorbed by the deeper soil particles, the  $\text{NH}_3$  emission decreased at 80% FC as compared to that at 20%. This seemed to occur about 7 days following incubation (Fig. 9). As the  $\text{NH}_4^+$  source was depleted after about 14 days, the  $\text{NH}_3$  volatilization rate declined until about 28 days (Fig. 9). For two of the tested soils amended with all of N sources the  $AQ$  values were basically greater than the IMP, but not for the BMS and QFS soils amended with  $\text{NH}_4\text{NO}_3$ . At 20°C, the  $AQ$  values increased from Day 7 through Day 28 (Fig. 9). At 11°C, the  $AQ$  values were close to zero during the entire incubation period. Hence at this low temperature, the  $\text{NH}_3$  volatilization from the QFS soil amended with  $\text{NH}_4\text{NO}_3$  was essentially not influenced by the soil moisture regimes. At 11°C,  $\text{NH}_3$  volatilization rates were quite low from the BMS, KGL, and WSL soils amended with  $(\text{NH}_4)_2\text{SO}_4$ ,  $(\text{NH}_2)_2\text{CO}$ , or  $\text{NH}_4\text{NO}_3$ , and this rate was also low from the QFS soil amended with either of  $(\text{NH}_4)_2\text{SO}_4$  or  $(\text{NH}_2)_2\text{CO}$ . Similarly, the BMS soil amended with  $\text{NH}_4\text{NO}_3$  had one IMP at 11°C (Fig. 10) but the other soils didn't have IMP in this research.

#### 4 Conclusion

Management options to reduce  $\text{NH}_3$  emissions from agricultural N fertilizer sources are highly desirable to minimize the negative environmental impacts associated with this form of N losses from agricultural uses of N fertilizers. The moisture quotient ( $Q$ ) in this study was the ratio of  $\text{NH}_3$  emission rates at 20 and 80% FC. Thus,  $Q$  provides a quantitative expression of effects of variable soil water regimes on  $\text{NH}_3$  emission and also describes the dynamics of  $\text{NH}_3$  emission over time. Results of this study revealed that  $\text{NH}_3$  volatilization was significantly influenced by the N sources. Ammonia emission was greater from the soils amended with  $(\text{NH}_4)_2\text{SO}_4$  or urea, as compared to that of the soils amended with  $\text{NH}_4\text{NO}_3$ . Low soil water regime (20% FC) significantly increased  $\text{NH}_3$  volatilization across all N sources. The maximum  $Q$  values across all soils and incubation duration were 19.3, 48.3 and 112.9 at 11, 20 and 29°C, respectively. Furthermore, only the QFS soil amended with  $\text{NH}_4\text{NO}_3$  demonstrated two IMP points and the BMS had one IMP point indicative of similar  $\text{NH}_3$  emission rates at either 20 or 80% FC soil water regimes. Ammonia emission from inorganic N fertilizers used for agricultural production can be minimized by maintaining soil water regime near field capacity level, particularly during the initial 10–14 days following the N application. Reduction in  $\text{NH}_3$  emission from agricultural sources is able to improve air quality or, at least, to minimize the deterioration of air quality. In addition to the environmental benefits, decreasing  $\text{NH}_3$  emission



**Fig. 10** The active moisture quotient ( $AQ$ ) for the rates of ammonia volatilization from the BMS soil amended with  $\text{NH}_4\text{NO}_3$  at 11, 20, or 29°C

from agricultural practices economic benefits by way of enhanced N uptake efficiency by minimizing gaseous losses, which lowers the plant available N. Moreover, the reduction in NH<sub>3</sub> emission is beneficial to growers, since it should enhance N uptake and thereby lower the cost of the N input.

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