

Identification of Factors Most Important for Ammonia Emission from Fertilized Soils for Potato Production Using Principal Component Analysis

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Abstract

Ammonia (NH₃) emissions from fertilized soils are a costly problem that is undermining agricultural and ecological sustainability worldwide. Ammonia emissions from crop production have been reliably documented in recent years. However, insufficient efforts have been made to determine the factors most influential in facilitating NH₃ emissions. The goal of this study was to identify the principal factors facilitating NH₃ emissions from fertilized soils for potato production by means of principal component analysis (PCA). A dataset consisting of 14 different variables and 600 determinations of NH₃ emission rates was geometrically classified into 5 zones, and then analyzed with the PCA technique. The data used in this analysis originated from an incubation experiment involving four major potato production soils (two from Washington State and two from Florida, USA), five N sources, two soil water regimes, three incubation temperatures and five measurement dates of NH₃ emission rates during 28 days of incubation: Day 1, 3, 7, 14, and 28. Ammonia emission rates was classified into five distinct zones. In

the five zones the total variance in NH₃ emission was accounted for as follows: soil particle size distribution, electrical conductivity (EC), field capacity, and bulk density, 47%; fertilizer sources, 15%; soil pH, 12%; and soil temperature and the soil water regime 9%. The effects of the principal components on NH₃ emission in descending order were as follows: soil type > fertilizer source > soil pH > soil temperature and water regime. Therefore, NH₃ emissions could be reduced potentially with amendment of coarse textured agricultural soils to reduce their bulk density, selection of fertilizers to lessen those with the ammonium compounds, use of amendments to lower soil pH, and optimal water management.

Keywords: Ammonia volatilization • Fertilized soils • Principal component analysis (PCA) • Soil type.

Abbreviations: EC, electrical conductivity; FC, field capacity; nBTPT, N-(n-butyl) thiophosphoric triamide; PC, principal component; PCA, Principal component analysis.

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1. Introduction

Ammonia (NH_3) is the third most abundant nitrogen (N) gas after N_2 and N_2O in the atmosphere. Crop and livestock production contributes approximately 90% of total NH_3 emitted into the atmosphere (Schlesinger and Hartley, 1992; Ferm, 1998). In Western Europe, about 92% of all emitted NH_3 was traced to agricultural origins (Kirchmann et al., 1998). Fertilization of crops alone contributes more than 50 percent of the global emission of NH_3 (FAO, 2001). Nitrogen loss to the environment has been a major concern for many decades (Ma et al., 2008). Reductions in NH_3 emission from agricultural production practices are imperative to enhance N utilization efficiency and improve air quality (Breeman et al., 1982; Buijsman et al., 1987; Fangmeier et al., 1994; Kirchmann et al., 1998; Gay and Knowlton, 2005; Aneja et al., 2006). Indeed since the mid-1800s, some attention has been given to the development of effective strategies to minimize NH_3 emission (Sprenkel, 1839; Boussingault, 1851; Bussink and Oenema, 1998). Major factors which influence the extent of NH_3 emission have been shown to include the N application rate (Vlek and Stumpe, 1978), N source (Fenn and Kissel, 1973), soil pH (Bremner and Douglas, 1971; He et al., 1999; Liu et al., 2007), temperature (Liu et al., 2007), soil water regime (Fox and Hoffman, 1981; Liu et al., 2007), and soil organic matter content (Paulson and Kurtz, 1969). To reduce NH_3 emission from livestock production operations, shallow manure slurry injection and urease inhibitors have been employed (Hansen et al., 2003; Singh et al., 2009). Urease inhibitors such as N-(n-butyl) thiophosphoric triamide (nBTPT) are recommended to control nitrogen loss from urea via NH_3 emission (Watson et al., 1994 and Watson et al., 2008; Sanz-Cobena et al., 2008). The reduction of NH_3 emission from fertilized soils is achievable by application to paddy rice at panicle initiation compared to broadcasting at transplanting is 50 percent (FAO, 2001). Fenn et al. (1981) found that soluble calcium and magnesium reduced N loss via NH_3 emission. Fenn and Hossner (1985) comprehensively summarized the effects of fertilizer type, application method, soil properties, and temperature and soil water on NH_3 emission. However, the magnitude of influence by each of the above factors within a given system is not clearly understood. Also, the effects of soil type including particle size distribution, bulk density, electrical conductivity, and field capacity on NH_3 emission have not been fully investigated.

The identification of key variables that might be managed to reduce NH_3 emissions and improve air quality as well as N uptake efficiency by crops is far from simple and presents a complex problem in statistical analysis. Principal component analysis (PCA), originated by Pearson (1901) and further developed by Hotelling (1933), was applied extensively in research on analysis of data involved in telephonic communications and engineering in 1960s (Rao, 1964; Gnanadesikan, 1977). Since 1970s, PCA has been used in chemistry to gain insight into spectral data of systems containing a mixture of chemical compounds that contribute to a spectral signature (Beauchemin et al., 2002). The power of this multivariate statistical tool to interpret large datasets was demonstrated by Malinowski (1991) and Beauchemin et al. (2002) in the identification of principal factors in datasets

involving absorption and emission spectra, gas chromatography, mass spectrometry, and nuclear magnetic resonance spectroscopy.

During the 1990s, the PCA approach was successfully applied to characterize the distribution of vegetation (Hirosawa et al., 1996), protein dynamics (Balsera et al., 1996) and molecular biology such as DNA microarrays (Raychaudhuri et al., 2000). Recently, the PCA approach was effectively employed in water quality analysis (Ouyang, 2005). The above studies have demonstrated the application of PCA to reduce dimensionality and to delineate the most important factors responsible for the most variation and thus extract the essential factors from large and multivariate data sources. Therefore, it seemed important to apply the PCA analysis to sort out the major factors contributing to NH_3 emissions from soil-applied N fertilizers in irrigated potato production systems and that is the main thrust of this study. The objectives of this study were: (i) to identify the principal factors affecting NH_3 emissions from fertilized soils used for potato production, and (ii) to assess the differential impact of these factors on NH_3 emission.

2. Materials and Methods

NH_3 emission rates in this study vary widely and range from 0.1 to 6183.4 g N ha⁻¹ d⁻¹. There is almost nothing for the control without N fertilization and the treatment of KNO_3 . However, more than 70% of NH_3 emissions from the other three treatments amended with either NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, or urea are completed in the first week after N fertilization (Liu et al., 2007). The statistical results of a dataset with such large variability may be seriously distorted due to the huge heterogeneity in the measured observations. To avoid such a distortion, the dataset needs to be divided into groups for being analyzed by the PCA technique. Classification, which involves the detection in the relationships between the variables, is employed for this purpose. In this study, geometric classification is used for dividing a dataset into different groups. In geometry, the data can be considered as having a homogenous property when the classified data share an analogous slope (Shani et al., 2005). The method for classification based on slopes of curves is defined as the geometric classification of data. Geometric classification is a process of dividing a dataset into mutually exclusive groups in which the data are close together within a group but quite distant between and among the different groups. The numerical separation between different groups is measured with respect to a specific variable such as the NH_3 emission rate, which we employed in this study.

2.1 Data Source

The dataset used in this study included 600 measurements of NH_3 emission rates (g N ha⁻¹ day⁻¹) in a laboratory study with the following four soils: Biscayne Marl Soil (loamy, carbonatic, Hyperthermic, shallow Typic Fluvaquents), Krome Gravelly Loam (loamy-skeletal carbonic, hyperthermic Lithic Udorthents), Quincy Fine Sand (Mixed, Mesic Xeric Torripsamments), and Warden Silt Loam (Coarse-silty, mixed, Mesic, Xerollic Camborthids). The

major potato production regions in Florida are represented by the first two mentioned soils, while those in the State of Washington are represented by the third and fourth mentioned soils. Four N sources commonly used in potato production in these states were KNO_3 , NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_2)_2\text{CO}$ and a control treatment (without N application) was also evaluated.

The investigation of ammonia emission involved the following variables: (i) three incubation temperatures, i.e., 11, 20, and 29°C, which are the minimum, mean, and maximum temperatures of the Washington potato production season, respectively, and the corresponding temperatures of the Florida potato production season are similar; (ii) two soil water regimes: 20% and 80% of field capacity (FC), which are the two soil moisture extremes before and after each irrigation event, respectively; and (iii) sampling at 5 times after fertilizer application, i.e., 1, 3, 7, 14, and 28 days. Thus, a total of 600 combinations ($4 \times 5 \times 3 \times 2 \times 5$) of factors were performed each in triplicate. Every datum was the average of the three replications in this study. Characteristics of the soils involved and detailed descriptions of the methods used can be found in Liu et al. (2007).

In brief, NH_3 volatilization was measured by trapping NH_3 with sponges spiked in a trapping solution, containing concentrated phosphoric acid, glycerol, and deionized water. The concentration of $\text{NH}_4^+\text{-N}$ was analyzed using an Autoanalyzer 3 (Bran+Luebbf GmbH, Werkstrasse, Norderstedt, Germany, www.bran-luebbe.de) according to US-EPA Method 350.1 (EPA, 1993).

2.2 Geometric Classification

The NH_3 emission rates with 600 data points from the fertilized soils were sorted from maximum to minimum and numbered from 1 to 600 using Microsoft Excel 2007. The emission rates were plotted on the y-axis and the data numbers were plotted on the x-axis. Then the data points were regressed to the following exponential function.

$$\begin{aligned} y &= 2032.6e^{-0.0149x} \\ R^2 &= 0.99 \\ p &< 0.0001 \end{aligned} \quad (1)$$

Based on the derivative principle in mathematics, any nonlinear curve can be approximated as a number of linear curves with different slopes; in addition a nonlinear curve can be fitted in a piecewise manner (Shani et al., 2005). The data in this study were classified based on the trend line of the NH_3 emission rate vs. the datum number by means of a 2-step procedure, as follows. In step 1: the dataset was divided into three zones because the trend line has three distinct zones, i.e., a steep linear zone, a curvilinear transition zone, and a flat linear zone (Fig. 1). Thus, there are two linear zones and one non-linear zone (curvilinear transition zone). In step 2: the curvilinear transition zone was further grouped into three quasi-linear zones with different slopes. Therefore, the entire range of NH_3 emission rates vs. data numbers was divided into five separate linear or quasi-linear zones with slope ranges of: ≤ -200 for data points 1 through 20, ≤ -20 for data points 21 through 66, ≤ -2 for data points 67 through

220, ≤ -0.2 for data points 221 through 374, and ≤ -0.02 for data points 375 through 600. The assumption used in this classification was that all of the data points in each separate zone have a very similar slope but that the different consecutive zones have distinct slopes differing by 10-fold. The assumption for this classification can also be different. For example, the distinct slopes may differ by 5- or 20-fold between every two different consecutive zones. However, the former scenario (5-fold) has too many zones that are too complicated to be understood. The latter scenario (20-fold) has too few zones that over-simplify the information the dataset has and this scenario can't be fully understood. Thus, the distinct slopes between every two consecutive zones with 10-fold numerical separation are considered suitable in this study.

2.3 Analysis Procedures

Fourteen variables were included in this analysis (Table 1). The PRINCOMP package from the Statistical Analysis System (SAS) software (version 9.1.3, SAS Institute, 2009) was used to perform the PCA analysis in this study. The PCA analysis was conducted on the standardized variables using a covariance matrix (Ouyang, 2005; Ouyang et al., 2006). In previous studies involving this statistical tool, a cumulative variance was considered as statistically significant with that variance was greater than 75% (Ouyang, 2005), 80% (Zhao, 2003) or 85% (Hao et al., 2003). In this study, a cumulative variance that is greater than 80% was considered as significant statistically. This slightly conservative criterion was selected because the soils used were heterogeneous and the treatments were diverse.

3. Results and Discussion

3.1. Geometric Classification of Observation Dataset

Based on a classification by geometric means, the nonlinear curve of the NH_3 emission rates across all samples was represented as the five linear lines described above. Thus the entire NH_3 emission rate curve was segmented into 5 separate range zones based on major differences in the slopes of the 5 segments as shown in Table 2 and Fig. 1.

Based on the range of NH_3 emission rates in each of the 5 zones (see Table 2), there were five corresponding minimum and maximum values of NH_3 emission rates. By taking each maximum value as the y-coordinate for each zone's linear function, then the quotient of delta y to delta x in each zone was the slope of the line segment. Thus the line segment in each the five zones (Fig. 2) could be described as follows:

$$\begin{aligned} y_A &= -208.5100x + 5252.8 \\ R^2 &= 0.84 \\ p &< 0.0001 \end{aligned} \quad (2)$$

$$y_{B1} = -20.8560x + 2018.2$$

$$R^2 = 0.97$$

$$p < 0.0001 \quad (3)$$

$$y_{B2} = -3.5523x + 795.4$$

$$R^2 = 0.93$$

$$p < 0.0001 \quad (4)$$

$$y_{B3} = -0.4789x + 171.7$$

$$R^2 = 0.90$$

$$p < 0.0001 \quad (5)$$

$$y_C = -0.0211x + 12.3$$

$$R^2 = 0.95$$

$$p < 0.0001 \quad (6)$$

Table 1. Variables in the investigation of principal factors governing ammonia emissions from fertilized soils used for potato production in Florida and Washington State.

Fertilizers applied (kg N ha ⁻¹):	
	NH ₄ -form: 0–75.0
	NO ₃ -form: 0–75.0
Soil particle size distribution (g kg ⁻¹):	
	Clay: 19–175
	Silt: 112–732
	Sand: 93–869
Soil basic characteristics:	
	Bulk density (g cm ⁻³): 0.88–1.43
	Electrical conductivity (EC, μS/cm): 49–457
	Field capacity (FC, g/100 g soil): 24.74–60.45
	Organic matter (%): 0.41–1.79
	pH: 6.46–7.69
Sampling time (d): 1, 3, 7, 14, and 28	
Soil water regime (% FC): 20 and 80	
Temperature (°C): 11, 20, and 29	
Rate of ammonia volatilization (g N ha ⁻¹ day ⁻¹): 0.1–6183.4	

Table 2. Classification of 600 determinations of rates of NH₃ emission in an incubation experiment involving four types of soils, four N sources plus a control without fertilization, three incubation temperatures, and two soil water regimes.

Zone	Number of data	Data No. range	Slope	NH ₃ emission Rate range -----g N ha ⁻¹ day ⁻¹ -----	Average rate	Data No.	
						20%FC	80%FC
A	20	1–20	-208.5100	1700.9–6183.4	3064.4	90.0	10.0
B1	46	21–66	-20.8560	728.1–1700.8	1111.0	71.7	28.3
B2	154	67–220	-3.5523	81.7–728.0	285.7	51.7	48.7
B3	154	221–374	-0.4789	5.4–81.6	29.2	44.2	55.8
C	226	375–600	-0.0211	0.1–5.3	2.1	45.1	54.9

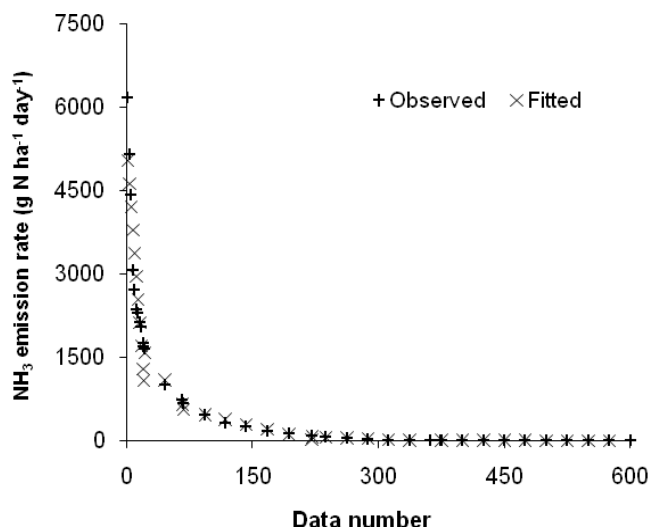


Fig. 1. The observed curve of 600 NH₃-emission rates on fertilized soils from Florida and Washington State and its five linearly fitted zones: A, B1, B2, B3, and C. To make the figure clearer the data were thinned. The data-thinning was done by retaining the first and last points in each linear line and retaining data at increment of 2 for zone A, and increment of 25 for the zones B1, B2, B3, and C. Thus, 600 data points were reduced to 39.

Accordingly, we developed a fitted matrix from Eqs. 2 through 6. Subsequently, a graph was plotted based on the observed and fitted data, which required only 39 data points as described below. The data-thinning was accomplished by retaining the first and last data points in each zone. In addition every second data point was retained in Zone A, and every 25th data point was retained in the remaining zones; i.e. B1, B2, B3, and C. Thus the 600 data points were reduced to just the 39 as shown in Fig. 1.

The mean NH₃ emission rate in zone A was the highest at 3,064.4 g N ha⁻¹ day⁻¹ and the earliest to occur with a mean of 2.0 days of incubation. In contrast, the mean NH₃ emission rate in zone C was the lowest at 2.1 g N ha⁻¹ day⁻¹ and the last to occur with a mean of 13.8 days of incubation. Both mean NH₃ emission rates and mean days of incubation were intermediate in Zones B1, B2, and B3 (see Table 2). Based on the distributions of NH₃ emission rates and days of incubation, NH₃ emissions in Zones A, B1, B2, B3, and C were designated as maximum, fast, medium, slow, and minimum, respectively.

Since high NH₄⁺ concentrations are one of the major drivers of rapid NH₃ emissions from the soils, split applications of N fertilizers should be highly recommended in order to minimize NH₃ emissions to improve N uptake efficiency and to protect air quality (Sowers et al., 1994). Additionally, Table 2 indicates that 90.0, 71.7, 51.7, 44.2 and 45.1% of the data of Zones A, B1, B2, B3, and C, respectively, were from dry (20% FC) soil. In the medium zone, Zone B2, approximately half of the data points were contributed from either the 20% FC soil water regime or the 80% FC soil water regime. However, for the maximum Zone A and the fast Zone B1, 90 and 71.7%, respectively, of the data points were contributed by the 20% FC soil water regime. This

Table 3. Variables in the investigation of principal factors governing ammonia emissions from fertilized soils used for potato production in Florida and Washington State.

Factor	Correlation Coefficients				
	Zone A	Zone B1	Zone B2	Zone B3	Zone C
Bulk density	0.0443	0.0564	-0.1227	0.1178	-0.0201
Clay content	0.0367	-0.0494	0.1612*	-0.1157	0.0374
Electrical Conductivity	-0.0525	-0.0562	0.1352	-0.1366†	0.0337
Field capacity	-0.0741	-0.0581	0.1214	-0.1353†	0.0270
Incubation Time	-0.4088†	-0.3353*	-0.1515†	-0.0267	-0.5105***
NH ₄ ⁺ -N rate	0.2709	0.0210	0.1074	0.3873***	-0.0575
NO ₃ -N rate	-0.2709	-0.0210	-0.1074	-0.2052*	0.2223**
Organic matter	0.3810†	-0.0100	0.1430†	-0.0124	0.0169
pH	0.4143†	0.0047	0.1523†	0.0023	0.0292
Sand content	0.0536	0.0569	-0.1148	0.1143	-0.0159
Silt content	-0.0790	-0.0581	0.0991	-0.1105	0.0092
Soil water regime	-0.2634	0.0292	-0.0757	-0.0166	0.0769
Temperature	-0.0240	0.0589	0.0971	-0.1307	0.0495
$r_{0.10, df}^{\dagger\dagger}$	0.3783	0.2455	0.1333	0.1333	0.1101
$r_{0.05, df}$	0.4438	0.2905	0.1586	0.1586	0.1312
$r_{0.01, df}$	0.5614	0.3758	0.2076	0.2076	0.1722
$r_{0.001, df}$	0.6788	0.4687	0.2901	0.2901	0.2423

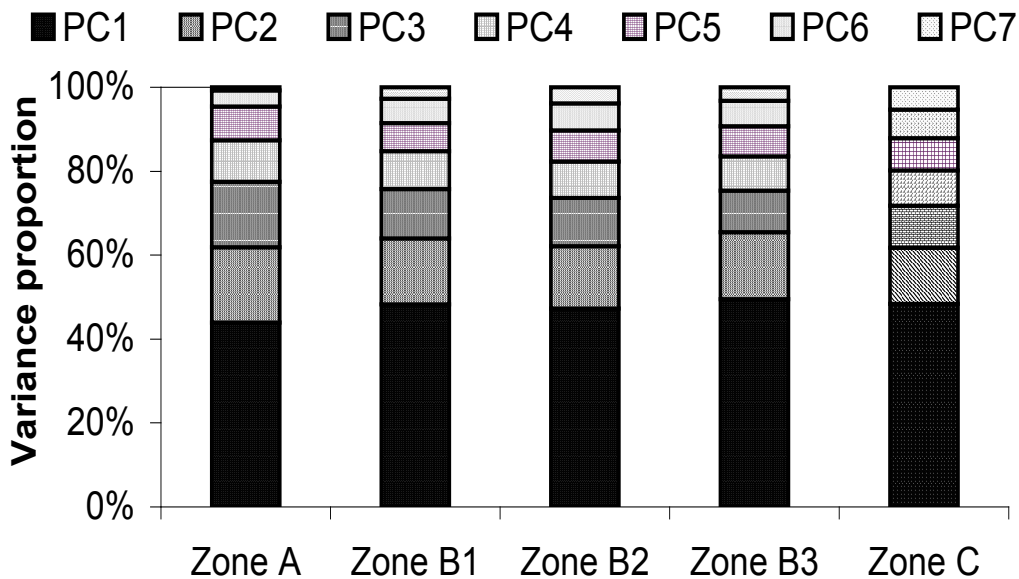


Fig. 2. Soil type, the first principal component (PC1) in each of the five zones contributed approximately to 50% of the variance in NH₃ emission. The first four PCs basically explained up to 87.1% of variance. The first four PCs are as follows: PC1, soil type; PC2, NH₄⁺ and NO₃⁻; PC3, soil pH; and PC4, temperature and soil moisture.

observation suggests that dry soil was a major factor associated with high NH_3 emission rates. Given the low soil water regime the transport of NH_4^+ ions from the surface soil into deeper soil was strongly restricted. Therefore, NH_4^+ ions formed in the surface soil were more vulnerable to conversion to NH_3 , which in turn was readily subject to volatilization. These results show that the establishment and maintenance of an appropriate soil - water regime is essential for controlling N loss via NH_3 emission from the fertilized soils tested in this study.

3.2. Correlations Between NH_3 Emission Rate and Other Factors

Correlation analysis was done for each of the five zones (Table 3). Ammonia emission rates in Zone A were rapid (see Table 2). The major factors that impacted the NH_3 emission rate were pH followed by duration of incubation. The time range for Zone A was only 3 days with frequencies of NH_3 determinations of 60.0% and 40.0% for days 1 and 3, respectively. Organic matter also influenced NH_3 emission rates significantly at $p < 0.10$ (see Table 3).

The NH_3 emission rates in the fast emission zone (B1) ranged from 728.1 to 1700.8 $\text{g N ha}^{-1} \text{d}^{-1}$ with an average of 1111.0 $\text{g N ha}^{-1} \text{d}^{-1}$ (see Table 2). Within this zone only incubation time had a statistically significant impact on the NH_3 emission rates ($R = -0.3353$) at $p < 0.05$ (see Table 3). In the medium emission zone (B2), clay content showed significant impact on NH_3 emission rates at $p < 0.05$; while the impacts of incubation time, organic matter and pH were significant at $p < 0.10$. In Zone B3, the slow emission zone, the time distribution primarily spanned the first two weeks. The 50th and 75th percentile of time distribution in this zone occurred in the first 7 and 14 days, respectively. The NH_3 emission rates in this zone were low but were strongly influenced by N source ($p < 0.001$), and weakly influenced by electrical conductivity ($p < 0.10$) and by % of field capacity ($p < 0.10$) (see Table 3).

The very low NH_3 emission rates in Zone C ranged from 0.1 to 5.3 $\text{g N ha}^{-1} \text{day}^{-1}$ with an average of 2.1 $\text{g N ha}^{-1} \text{d}^{-1}$ and a mode time of day 28, which occurred almost in one third of the time period. In this zone, NH_3 emission rates decreased significantly with time. NO_3^- -N had a significant positive correlation with NH_3 emission rates in Zone C, but not in any other zone (see Table 3). This observation might be attributed to inhibition of nitrification by high NO_3^- -N concentration. This inhibition would have caused the presence of NH_4^+ -N for a prolonged period leading to an increase in NH_3 emission rates. Gunderson et al. (1998) and Carpenter-Boggs et al. (2000) discovered that N fertilization including NO_3^- -N decreased net N nitrification in soil significantly.

3.3. Principal Components (PCs) Significantly Affecting Ammonia Volatilization

Several methods are used to plot PCA results. For example, some researchers plot eigenvalues against principal components (Cattell, 1966; Raychaudhuri, 2000; Jolliffe, 2002). In this study, we chose to evaluate the variance proportion of each of the principal components because the eigenvalue ranges were dif-

ferent for the five zones. Accordingly, the variance proportion was an appropriate criterion to compare among the five zones. Table 2 shows that the average NH_3 emission rate in Zone A was 1459-fold greater than that in Zone C. Indeed, NH_3 emission rates differed substantially. In these various zones, the first four PCs, i.e., soil type, N source, soil pH, and soil temperature/moisture factors, contributed more than 80% of variance (see Fig. 2). Therefore, the four PCs across the five zones were considered as the most substantial factors governing NH_3 emission from the fertilized soils in this study.

Examination of these histograms in Fig. 3 reveals that in each of the five zones clay, silt, sand, soil bulk density, field capacity, and electrical conductivity had large eigenvectors. The eigenvectors were essentially regression coefficients for the corresponding variables (Griffith, 2004). For example, the eigenvectors for the variable FC in PC1 were 0.40, 0.37, 0.37, 0.37 and 0.38 for Zones A, B1, B2, B3 and C, respectively. This result means that the regression coefficients between FC and NH_3 emission rates were 0.40, 0.37, 0.37, 0.37 and 0.38 in PC1 for the corresponding zones (see Fig. 3). These regression coefficients were always the largest or second largest values in PC1 for each of Zones A, B1, B2, B3 and C. The aforementioned six variables in each of the five zones are the signature of the soil type. Accordingly, soil type was the most important factor governing NH_3 emission from fertilized soils.

Thus, PC1 symbolized the identity of the soil type in the five zones. In Zone A, clay, silt, sand, bulk density, FC, and EC had the same weight with absolute values of 0.40, but sand and bulk density eigenvectors were negative. The sand content of the soils influences the bulk density as is evident from increases in bulk density of the soils with increasing sand content. For example, across the four soils evaluated in this study, the bulk density of Quincy Fine Sand (86.9% sand) was 1.43 g cm^{-3} , while the bulk density of Biscayne Marl Soil (9.3% sand) was 0.88 g cm^{-3} . Sand does not have many functional groups that can bind NH_4^+ ions. Hence, a soil that contains greater sand content necessarily has lower potential to retain NH_4^+ ions. Thus, NH_3 volatilization might be greater from sandy soils than from fine textured soils.

The variables including clay, silt, FC, and EC had positive regression coefficients in PC1 across the five zones. Clay and silt particles have much greater specific surface areas and more functional groups than sand. Therefore, in this study the former fractions had much greater potential to retain NH_4^+ ions than the sand fraction. Consequently, NH_3 emission rates tend to be lower in fine textured soils than in sand (Liu et al., 2007). The presence of clay and silt forms much smaller pores or capillaries than sand alone. This relationship is the basic reason why clay or silt soils have much greater FC than sandy soils (Minasny and McBratney, 2003).

Field capacity has positive regression coefficients with PC1 (see Fig. 3). This statistical outcome might be explained by the fact that soils with greater FC generally contain greater proportions of clay and silt than soils with lower FC. Accordingly, soils with high water holding capacity might retain greater amounts of NH_4^+ and thereby decrease NH_3 emission. Greater EC values were indicative of presence of greater amounts of metals and other ions occupying the functional groups of soil particles. Con-

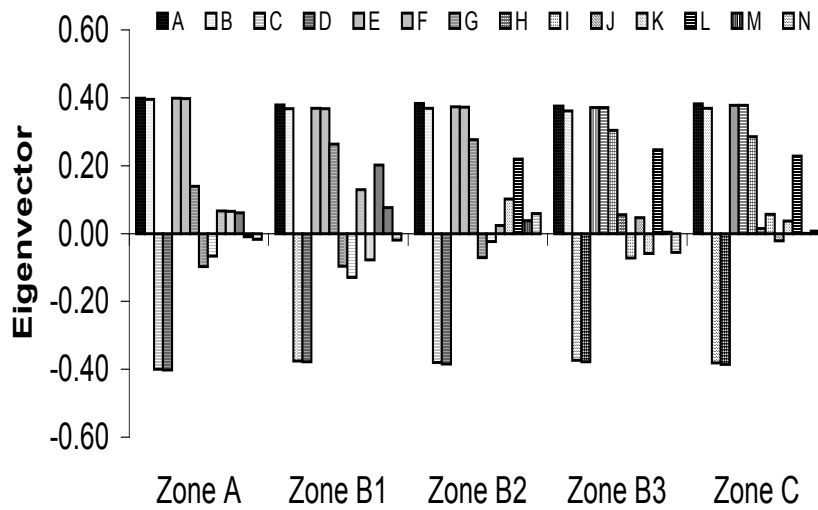


Fig. 3. Soil particle size distribution (i.e., clay, silt, and sand), bulk density, field capacity, and electrical conductivity, in the five zones, always had the 6 greatest absolute eigenvectors (i.e., characteristic vector) among the 14 variables. For the legend: A = clay content; B = silt content; C = sand content; D = bulk density; E = electrical conductivity; F = field capacity; G = organic matter; H = temperature; I = NH₄⁺-N rate; J = NO₃⁻-N rate; K = incubation time; L = pH; M = soil water regime; and N = NH₃ emission rate.

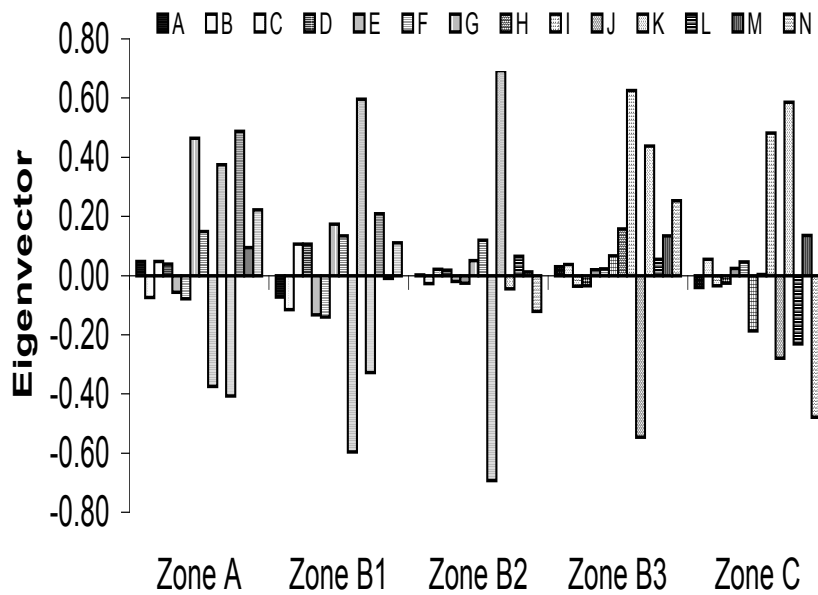


Fig. 4. Ammonium and nitrate, PC2, in the five zones, possessed the main absolute eigenvectors. For the legend: A = clay content; B = silt content; C = sand content; D = bulk density; E = electrical conductivity; F = field capacity; G = organic matter; H = temperature; I = NH₄⁺-N rate; J = NO₃⁻-N rate; K = incubation time; L = pH; M = soil water regime; and N = NH₃ emission rate.

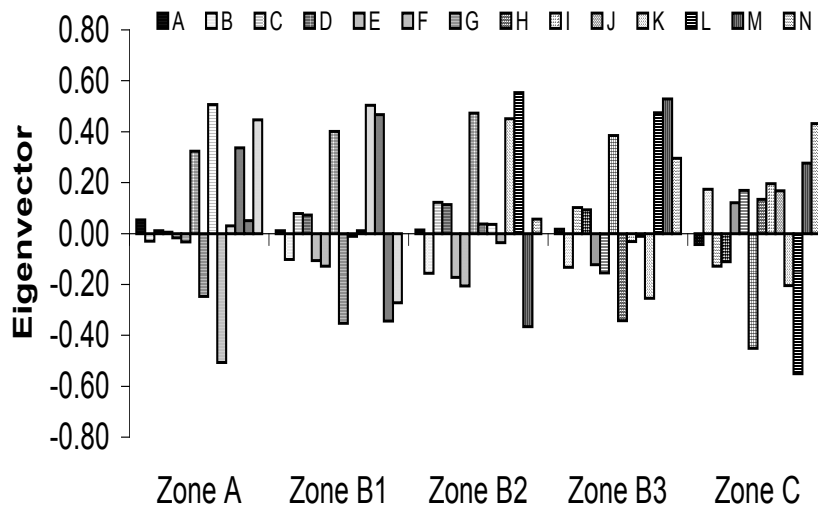


Fig. 5. Soil pH, PC3, in the five zones, was found to be the third factor. For the legend: A = clay content; B = silt content; C = sand content; D = bulk density; E = electrical conductivity; F = field capacity; G = organic matter; H = temperature; I = NH₄⁺-N rate; J = NO₃⁻-N rate; K = incubation time; L = pH; M = soil water regime; and N = NH₃ emission rate.

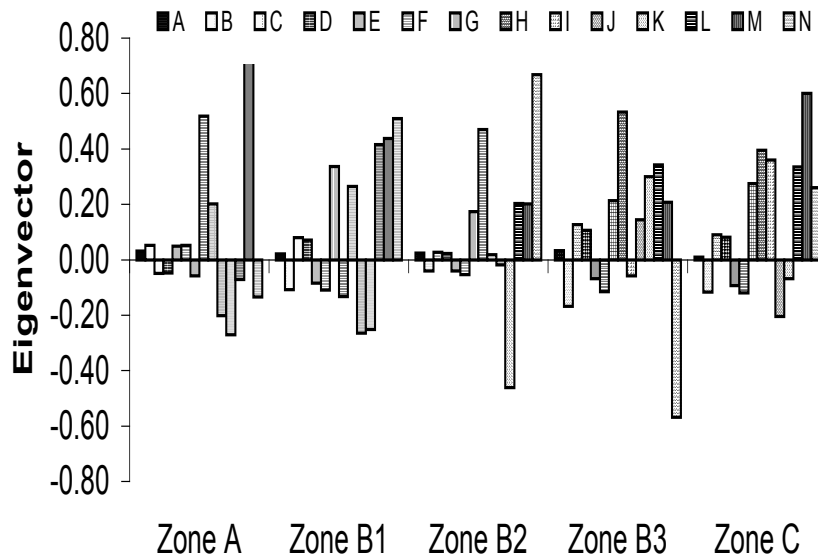


Fig. 6. The soil water regime and temperature, PC4, in the five zones, contributed to the preponderance of the variance of ammonia emission across the five zones. For the legend: A = clay content; B = silt content; C = sand content; D = bulk density; E = electrical conductivity; F = field capacity; G = organic matter; H = temperature; I = NH₄⁺-N rate; J = NO₃⁻-N rate; K = incubation time; L = pH; M = soil water regime; and N = NH₃ emission rate.

sequently, there were few functional groups available for sorption of NH_4^+ ions on the soil particles, thus, facilitating increased NH_3 emission.

The eigenvectors for the soil water regime in PC1 (soil type) were -0.01, 0.08, 0.04, 0.00 and 0.00 for the five zones (see Fig. 3). These values were much lower than those for FC. This was quite expected since FC was reflective of soil properties and affected NH_4^+ adsorption. Accordingly, there was a greater positive correlation between FC and NH_3 emission. However, the soil water regime impacted greatly on PC3 (Fig. 5) and on PC4 (Fig. 6) even though it impacted negligibly on PC2 (Fig. 4).

The contribution of soil pH to PC1 was rather weaker than to PC2 (ammonium and nitrate) and to PC3 (soil pH) in Zone A, PC3 and PC4 (incubation temperature and soil moisture) in Zone B1, PC3 in Zone B2, Zone B3, and Zone C (see Figs. 3 through 6). These results showed that pH was not always the most important factor affecting NH_3 emission rates; yet related publications categorize it as the most significant factor (He et al., 1999; Saffigna and Freney, 2002). This discrepancy might be attributed to the application of an advanced statistical tool in this study. This study demonstrated that soil particle size distribution characteristics had greater influence on NH_3 emission than the soil pH. Soil pH had little effect on NH_3 emission for PC1 in Zone A (see Fig. 3) because 62.7% of NH_3 emission in Zone A occurred on Day 1 soon after N was applied to the soils. The high NH_4^+ concentration in the soil solution favored greater NH_3 emission. Soil pH influenced NH_3 emission during the later period of incubation because by then the NH_4^+ concentration in soil solution had declined and its effect on NH_3 emission had diminished while the effect of pH had increased with time.

The influence of NH_4^+ and NO_3^- (PC2) on NH_3 emission, decreased in the order: Zones B1, B2, and B3 > Zone A \approx Zone C (Fig. 4). PC2 contributed from 12.9% to 17.9% to the total variances across the five zones. Accordingly, PC2 can be designated the "fertilizer" factor. The PC3 (soil pH) accounted for 9.6% to 15.5% of the total variances across the zones (see Fig. 5). The pH factor had regression coefficients of 0.34, 0.47, 0.55, 0.47, and -0.55 to the corresponding PC3 across all the zones, respectively. However, the contributions of the other variables differed with the zones. In Zone A, NH_3 emission rate, as well as concentrations of NH_4^+ and NO_3^- had relatively high values. Since the contribution of NH_4^+ and NO_3^- were accounted for in PC2, these factors were not considered in PC3. In PC3, the contribution of pH was significant across all zones (see Fig. 5), therefore, PC3 can be called the "pH" factor (see Fig. 5). PC4, temperature and soil moisture, showed a significant effect on NH_3 emissions across all zones. Hence, PC4 is considered as "temperature and soil moisture" factor (see Fig. 6).

The importance of soil pH, moisture, temperature, source and rate of N in influencing NH_3 emission has been reported by other investigations (Fenn and Hossner, 1985; He et al., 1999; Liu et al., 2007). The results of the current study demonstrated that soil particle size distribution, bulk density, FC, and EC also play a significant role in influencing NH_3 emission. Therefore, soil type exerts an important role in influencing NH_3 emission. However, this relationship was not recognized without the application of the sophisticated statistical analysis tool, PCA. Furthermore,

some investigations on NH_3 volatilization were conducted using only one soil type (Chantigny et al., 2004) which precluded the identification of the soil type as a major contributor to NH_3 emission.

4. Conclusions

An advanced statistical analysis technique, PCA, was applied to a dataset with 600 data points from an incubation experiment involving four soils from Florida and Washington State amended with four N sources plus a control without fertilization, subjected to two soil water regimes and incubated at three different temperatures. The dataset was geometrically classified into five distinct zones of significant differences in NH_3 volatilization rates. The geometrical classification indicated that NH_4^+ concentration and soil water regime were important factors influencing NH_3 emissions from soils to which N had been applied. The contribution of the PC1 through PC4 accounted almost 90% of the total variance across the five zones. PC1s through PC4s were described as soil type, N source, soil pH, and soil temperature/moisture factors, respectively. Ammonia emissions could be reduced substantially with amendment of coarse textured agricultural soils to reduce their bulk density, selection of fertilizers to decrease those with the ammonium compounds, use of amendments to lower soil pH, and optimal soil moisture.

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