Evaluation and Development of Cost Effective Method to Measure Ammonia Volatilization

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Abstract: Estimating the magnitude of ammonia (NH_3) volatilization loss under different conditions is important for proper fertilizer management. Both of the current field techniques used to trap volatilized NH_3 from soils amended with various N sources, and the techniques for the quantitative determination of NH_3, drain substantial, financial resources. This justifies re-evaluating existing popular methods, in order to develop a cost-effective field and laboratory method, to trap and determine volatilized NH_3 quantitatively and accurately. This study is designed to evaluate the effectiveness of (i) two absorbents (Phosphoric vs. Oxalic) in trapping volatilized NH_3, (ii) two extractants (KCl vs. deionized water) in removing absorbed NH_3, and (iii) two analytical procedures (Flow Injection Auto Analyzer vs. Ion Chromatography) in determining the concentration of NH_3 in extracts quantitatively, in most widely used two-passive flux methods. This evaluation was repeated under laboratory conditions, with two soils (light-textured Candler fine sand and medium-textured Ogeechee loamy sand) amended with various fertilizer N sources (Urea, Ammonium sulfate, Ammonium nitrate, Ammonium chloride along with an unamended control) and manure N sources (Chicken, Cattle, and Swine manures along with an unamended control) to identify the best combination of procedures to develop a cost effective method for determining volatilized NH_3. This presentation focuses on step-by-step evaluations of results obtained from several laboratory studies, so as to develop an effective method for field and laboratory scale determination of volatilized NH_3. Per our preliminary evaluation, the best combination of procedures would be to use 3% oxalic acid in acetone, to trap NH_3; deionized water, to extract the trapped NH_3; and Ion chromatography, to determine the concentration of NH_4-N in extract. This promises to reduce chemicals, cost, and labor, without sacrificing accuracy of measurement of volatilized NH_3.

Introduction:

- @ Estimating the magnitude of ammonia (NH_3) volatilization losses under different conditions is important for proper fertilizer management.
- @ Current field techniques to trap volatilized NH_3 from soils amended with various N sources and techniques used for the quantitative determination of NH_3 drain substantial financial resources.
- @ This justifies the need to re-evaluate current methods, prior to the development of cost effective field and laboratory methods to trap and determine the volatilized NH_3 quantitatively and accurately.
- @ Therefore, the current study was designed with the following objectives.

Objectives

To evaluate the effectiveness of the most commonly used

(i) two absorbents (Phosphoric and Oxalic) in trapping volatilized NH_3

(ii) two extractants (KCl vs. H_2O) in removing absorbed NH_3 and

(iii) two analytical techniques (Auto Analyzer vs. Ion chromatography) in determining the concentration of NH_3 in extracts quantitatively in most widely used passive flux methods.

Materials and Methods Used:

Soils:

1) Candler fine sand (pH = 6.8) – Lake Alfred, FL. [CFS]

2) Ogeechee loamy sand (pH = 5.2) – Savannah, GA. [OLS]

A. Treatment set up with inorganic fertilizer N sources and rates (0, & 200 kg ha^{-1}):

N sources	Treatment ID	Amt of N (mg) per 100 g of soil
Control	[T1]	00.0
Urea	[T2]	57.0
Ammonium sulfate	[T3]	42.0
Ammonium nitrate	[T4]	25.4
Ammonium chloride	[T5]	34.0

B. Treatment set up with organic manure N sources and rates (0, & 11.2 Mg ha^{-1}):

Control [T1]; Chicken manure [T2]; Cattle manure [T3]; and Swine manure [T4].

Set up of Incubation Study to Measure NH_3 Emission:

Incubation study was initiated by placing 100 g of Candler fine sand (pH = 6.8) from Lake Alfred, Florida, and Ogeechee loamy sand from Savannah, Georgia (pH =5.2), in 5cm diameter (1 L) mason jars. Soil samples in mason jars were amended on area basis with appropriate amounts various inorganic N sources to achieve amendments at the application rate of 0, 200 kg ha^{-1} in experiment 1. Experiment 2 was conducted with animal manures (chicken, cattle, and swine) at the application rate of 0, 11.2 Mg ha^{-1}.

Soils and respective amendments were mixed thoroughly and incubated at their respective field capacity level moisture contents (7 and 14% for Florida and Georgia soil respectively) through-out the study period. All treatments were triplicated.

Preparation of Acidified Sponge to Capture volatilized NH_3:

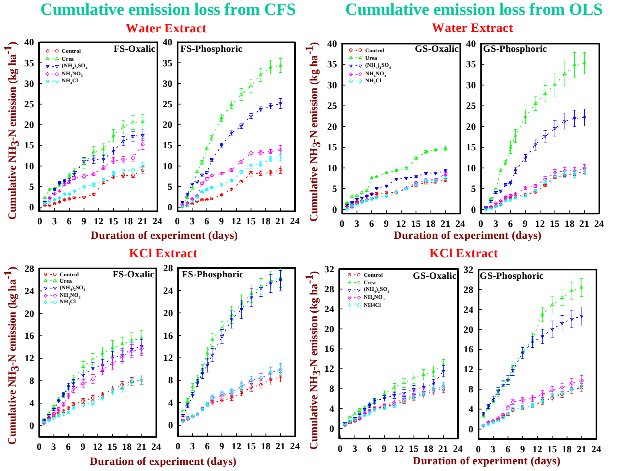
1a. Phosphoric-Glycerol: Sponges were made out by material used for seat-cushions, which were purchased from Jo Ann Fabrics in Savannah, GA, and cut into 2.5-cm diameter circles with an electric knife. The sponges were washed thoroughly in de-ionized water prior to transforming them into acidified sponges, to be used to capture emitted NH_3 from PL amended soils in mason jars. Acidified sponges were prepared by soaking and squeezing the sponges in various solutions in the following order: 1*M* H_3PO_4, 1*M* KOH, de-ionized water, and a mixture of 1*M* H_3PO_4 and Glycerol. The sponges were treated with first three solutions and squeezed thoroughly prior to treating them with a mixture of 1*M* H_3PO_4 and Glycerol. During the final stage of sponge preparation, the sponges were allowed to retain at least 3-5 mL of mixture of 1*M* H_3PO_4 and Glycerol to facilitate the capture of emitted NH_3 from the surface applied inorganic N sources.

1b. 3% Oxalic acid in Acetone: Acidified sponges were prepared by soaking and squeezing the sponges in various solutions in the following order: De-ionized water, and 3% oxalic acid in acetone. During the final stage of sponge preparation, the sponges were allowed to retain at least about 3-5 mL of 3% Oxalic-acetone solution to facilitate the capture of emitted NH_3 from the surface applied inorganic N sources.

Extraction of NH_4-N from Sponge: Sponges were extracted individually with 40 mL of either 2*M* KCl or de-ionized water and stored for determination of NH_4-N in the extract.

Measurement of NH_4-N in Extracts: Ammonium-N in KCl extract was measured by Flow Injection Analyzer (FIA) and Ammonium-N in de-ionized water by both Ion Chromatography and FIA.

Results and Discussion: Cumulative NH_3 emission loss from fertilizer N sources



Cumulative ammonia emission trend is in the following order: CO $(NH_2)_2$ > $(NH_4)_2$ SO_4 > NH_4NO_3 > NH_4Cl > Control.

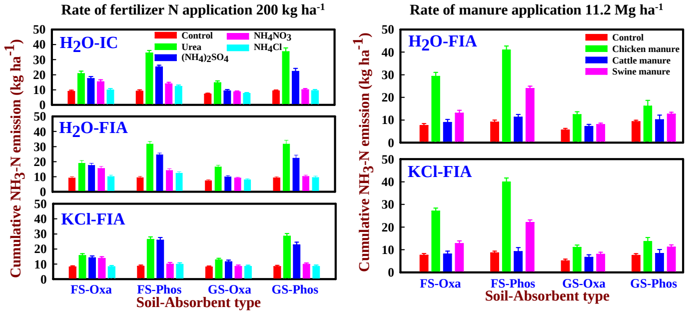
Greater ammonia emission is observed from light-textured soil (CFS) than that from medium-textured soil (OLS)

Greater ammonia absorption is observed in phosphoric acid treated sponge than the sponge treated with 3 % oxalic acid in acetone.

Concentration NH_4-N extracted by de-ionized H_2O is greater than that of concentration of NH_4-N extracted by 2 *M* KCl.

Analytical techniques (FIA & IC) employed for the determination of NH_4-N was compared only for samples extracted by H_2O from fertilizer N source study and the concentrations of NH_4-N are highly comparable. Concentration of emitted ammonia from untreated control treatment are practically similar irrespective of types of soil, absorbents, extractants, and analytical techniques

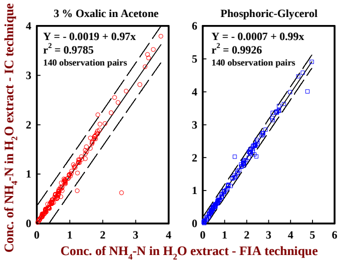
Comparison of cumulative NH_3 emission losses from fertilizer and manure N sources



Cumulative NH3 losses was in the following decreasing order:

- CO $(NH_2)_2$ > $(NH_4)_2$ SO_4 > NH_4NO_3 > NH_4Cl > Control.
- Chicken manure > Swine manure > Cattle manure > Control.
- Cumulative amount of NH_3 loss was greater in CFS that that of from OLS irrespective of soil types, N sources, absorbents, extractants, and techniques to used to estimate the concentration of NH_4-N.

Relationship between Conc. of NH_4-N by IC & FIA



Evaluation of Ion Chromatograph and Flow Injection Analyzer for the determination NH_4-N and Cost comparison

Concentrations of NH_4-N in de-ionized water extract measured by FIA technique and IC technique revealed that concentrations of NH_4-N are highly comparable irrespective of absorbent types used in this study

Components	IC	FIA	Commercial Labs
Chemicals	$ 0. 20	Chemicals	-
Vials	$ 0. 50	Other supplies	-
Labor	$ 0. 60	Labor	-
Instrument	$ 2. 00	FIA	-
Other supplies	$ 0. 70	IC	
Total / sample	$ 4. 00	Total / sample	$ 8. 00

Conclusion: Ammonia emission trend was in the following order: CO $(NH_2)_2$ > $(NH_4)_2$ SO_4 > NH_4NO_3 > NH_4Cl > Control for inorganic fertilizer N sources and Chicken manure > Swine manure > Cattle manure > Control for organic manures irrespective of types of soil, absorbent, extractant and analytical techniques. Evaluation revealed that phosphoric acid + glycerol mixture absorb greater NH_3 than 3 % oxalic acid in acetone solution. Similarly, evaluation also revealed that deionized water extract greater NH_4-N from NH_3 absorbed sponges than KCl. Concentrations of ammonia in de-ionized water extract measured through FIA technique and IC technique revealed that concentrations of NH_4-N are highly comparable irrespective of use of phosphoric acid or oxalic acid as absorbent. Concentration of ammonia in KCl extract could not be analyzed through Ion Chromatograph due to technical difficulties associated with masking effect of chromatogram of K^+ with NH_4^+. Thus, types of extractants could not be compared. Comparison of analytical cost (chemical, labor, and other supplies) revealed, that using ion chromatography is comparatively cheaper than FIA.

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