PERGAMON

Atmospheric Environment 36 (2002) 1087–1097

ATMOSPHERIC ENVIRONMENT

www.elsevier.com/locate/atmosenv

Characterization of ammonia emissions from soils in the upper coastal plain, North Carolina

Paul A. Roelle, Viney P. Aneja*

Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27695-8208, USA

Received 22 April 2001; accepted 26 June 2001

Abstract

A dynamic flow-through chamber system was used to measure fluxes of ammonia-nitrogen (NH_3-N, where NH_3-N = (14/17)NH_3) from soil surfaces. The research site was located in eastern North Carolina (35.9°N latitude; 77.7°W longitude) and measurements were conducted during spring and winter 2000, in order to assess the NH_3 source strength of intensively managed agricultural soils and the physiochemical properties which control these emissions. Soil temperature (T_{soil}), soil pH, soil moisture, total Kjeldahl nitrogen (TKN = organic N + NH_3-N + NH_4^+-N) were monitored throughout both research periods. Soil temperature was found to explain the largest variability in soil NH_3 emissions (Log_{10} NH_3-N Flux = $0.054T_{soil} + 0.66$; $R^2 = 0.71$), suggesting that an approach similar in design to the biogenic emissions inventory system land use and temperature model for NO emissions, might be effective for modeling biogenic NH_3 emissions. Soil nitrogen was also significant in predicting NH_3 flux [NH_3 Flux = 55.5(NH_3-N)−160, $R^2 = 0.86$; NH_3 Flux = 0.6(TKN)−410, $R^2 = 0.27$], but only after the two days with the heaviest rainfall were removed from the regression, emphasizing the role of soil moisture in controlling the transfer of gases across the soil/air interface. Soil pH remained relatively constant throughout both research periods and therefore did not serve as a useful predictor of NH_3 flux. A rain event, followed by a drying period produced a characteristic pulse in ammonia emissions. This pulsing phenomenon has been observed for other trace gases by various researchers. This research location was the site of a commercial hog operation, which allowed for the comparison of soil and lagoon emissions (lagoon emissions were based on an algorithm developed by Aneja et al. (J. Geophys. Res. 105 (2000) 11,535). An analysis of the source strengths confirmed that lagoon emissions are a larger flux source (average lagoon flux ~18,137 ng N m^{-2} s^{-1}; average soil flux ~54 ng N m^{-2} s^{-1}); however soil surfaces make up a larger fraction of a commercial hog operation than the lagoon surfaces, and as a result they cannot be neglected when developing and apportioning NH_3 emissions. A yearly average of ammonia emissions at this site revealed that soil emissions represent approximately 28% of the lagoon emissions. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ammonia; Dynamic flow-through chamber system; Soil emissions; Agriculture; Gas flux

1. Introduction

Ammonia (NH_3) is an important atmospheric trace species, both in terms of its effect on tropospheric chemistry and due to its impact on ecosystems. Ammonia, which is the most abundant alkaline species in the atmosphere, is critical to neutralizing acids formed through the oxidation of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) (Asman et al., 1998). When NH_3 is deposited onto the soil, it is both taken up by plants and converted by bacteria into nitrate (NO_3^-) (nitrification) (Lekkerkerk et al., 1995). The nitrification process forms hydrogen ions leading to acidification of the soil, leaching of NO_3^- to groundwater, and possible deficiencies of other plant nutrients such as potassium (K^+) and magnesium (Mg^{2+}) (Asman et al., 1998). In

---

*Corresponding author. Tel.: +1-919-515-7808; fax: +1-919-515-7802.

E-mail address: viney_aneja@ncsu.edu (V.P. Aneja).

PII: S1352-2310(01)00355-7

addition to acidification, excess nitrogen loading can lead to overenrichment of both land and water ecosystems. Further, excess N deposition can cause the above ground portion of the plant to grow rapidly, leaving the root system relatively smaller and weaker and more susceptible to disease and harsh weather conditions (Lekkerker et al., 1995).

Unlike oxidized nitrogen and sulfur compounds (NO_x and SO_x respectively), which are predominately emitted from industrial processes, NH_3 is primarily emitted by agricultural sources and therefore requires different control strategies (Sutton et al., 1993). A review of the current literature revealed that soil and plant emissions account for anywhere between 11% and 28% of the global NH_3 budget (Table 1). In North Carolina, which is currently the second largest pork producing state in the US, the percentage of ammonia emissions from swine is approximately 46% compared to the US average of 10% (Battye et al., 1994) (Fig. 1). Accurate inventories of NH_3 are needed to model both its transport and deposition (Misselbrook et al., 2000). Beyond quantifying this overall source strength and the effects to ecosystems, there needs to be an accurate budget and reliable source apportionment (i.e., animal houses, waste storage, land application, re-emission from soils) of nitrogen inputs into such systems (Aneja et al., 2000). Current inventories that are then used in air quality models are determined using emission factors (i.e., tons NH_3/animal/year or % NH_3-N emitted/ton of N-fertilizer applied), most of which are based on European studies. Therefore, the objectives of this study are to quantify and relate the soil NH_3 flux at an eastern North Carolina site to different environmental variables in the soil, and determine the source strength of these soil emissions. Moreover, the soil ammonia emissions will be compared and contrasted to ammonia emission measurements made over animal (swine) waste treatment and storage lagoons (Aneja et al., 2000).

2. Experimental

2.1. Sampling site and sampling scheme

The NH_3 flux measurements were made at the Upper Coastal Plain Research Station, located in Edgecombe County, North Carolina (see Table 2 for site/soil characteristics). This facility is operated with typical agronomic and husbandry practices for the respective crops and animals and contains approximately 178 ha, 101 of which are cropland soils. The facility also maintains a farrow-to-finish hog operation with approximately 1250 hogs on site. The waste from the animals (urine and feces) is flushed from the hog production houses into two uncovered anaerobic waste treatment and storage lagoons (a primary and secondary lagoon, total acreage ~1 ha). The effluent from these lagoons is periodically sprayed to the crops as a nutrient source. A corn crop was planted on 5 April 2000 and spring measurements began on 26 April and ended on 14 May 2000. Due to several rain events and equipment malfunctions, only 5 days were suitable for conducting the measurements, all of which are presented in Table 2.

Although the field sampled is typically sprayed with lagoon effluent, it was not sprayed during the 2000 measurement campaign and instead received approximately 146 kg N ha^{-1} on 24 May 2000. The corn crop was harvested on 21 August and the stalks were shredded and left on the soil surface. No cover crop was planted and the winter measurements were conducted from 13 to 19 December 2000. Rain events prevented measurements on two of the days, although measurements were made on the remaining 5, all of which are presented in Table 2.

NH_3 concentration measurements were made on 10 random sampling plots located within a 10 m radius of a mobile laboratory (Modified Ford Aerostar Van, temperature controlled to within the operating range

Table 1
Relative global ammonia source strengths (Tg N yr^{-1}) reported by several different researchers[a]

	Researchers source strengths (Tg N yr^{-1})		
Sources	Warneck (1988)	Schlesinger and Hartley (1992)	Dentener and Crutzen (1994)
Coal combustion	⩽2	2	—
Automobiles	0.2	0.2	—
Biomass burning	2–8	5	2
Domestic animals	22	32	22
Wild animals	4	—	2.5
Human excrements	3	4	—
Soil/plant emissions	15	10	5.1
Fertilizer losses	3	9	6.4
Oceans	—	13	7
Sum of sources	54	75	45

[a] Tg = 10^{12} g; adapted from Warneck (2000).

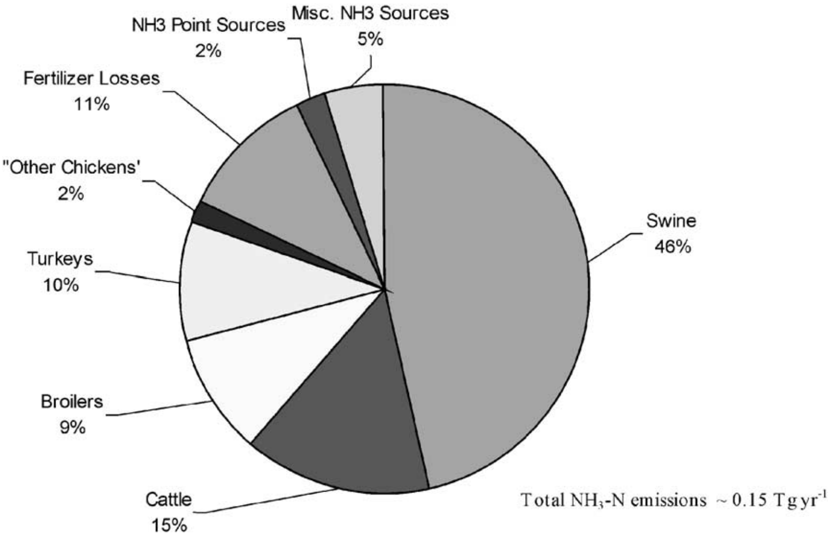

Fig. 1. Percent of ammonia-nitrogen from various sources in North Carolina.

Table 2
Site and soil characteristics for spring and winter 2000 measurement campaigns at the Upper Coastal Plain Research Station, Edgecombe County, NC[a]

Site: Upper Coastal Plain Research Station
35.9°N latitude
77.7°W longitude
Elevation: 35.5 m
Soil type: Norfolk loamy sand

Sampling period (N =)	Crop/fertilization	pH	%WFPS	N-content (μg g^{-1})			Soil temperature (°C)	NH$_3$ flux (ng N m^{-2} s^{-1})
				NH$_3$-N	NO$_3$-N	TKN		
5 April 2000	*Corn planted*							
26 April 2000 (33)		5.2	38.6	6.1	16.9	909	16.2±2.3	145.4±33.5
27 April 2000 (28)		5.2	40.5	7.7	17.7	1070	15.1±1.7	38.4±11.7
12 May 2000 (21)		5.1	24.9	7.0	19.2	963	28.4±3.0	271.1±135.1
13 May 2000 (20)		5.2	22.9	4.5	8.1	889	30.4±3.0	128.8±45.5
14 May 2000 (20)		5.5	24.3	5.1	5.4	806	28.6±2.2	90.3±13.6
24 May 2000	146 kg N ha^{-1}							
21 Aug 2000	*Corn harvested*							
13 Dec 2000 (29)		4.9	33.1	3.5	12.0	933	6.8±1.0	26.1±10.9
14 Dec 2000 (27)		5.2	39.9	8.5	11.1	1004	8.3±0.6	7.3±3.4
16 Dec 2000 (34)		5.2	28.6	3.0	5.3	941	8.8±1.5	9.6±5.7
18 Dec 2000 (29)		5.1	53.9	3.9	9.1	776	7.4±1.8	13.7±6.0
19 Dec 2000 (27)		5.3	35.8	2.4	8.6	737	6.9±1.9	3.4±43.1

[a] TKN (total Kjeldahl nitrogen) = organic N + NH$_3$-N + NH$_4^+$-N.

of the instruments). The sampling scheme consisted of measuring concentrations of NH$_3$ after the sample exited the dynamic flow-through chamber system. The system recorded 60-s, rolling averages of NH$_3$ concentrations. These values were then binned and averaged every 15 min. The 15-min binned averages were used in all flux calculations. N in Table 2 refers to the number of these binned averages (to also include soil temperature as discussed in Section 2.4).

A daily experiment consisted of placing the chamber on the stainless steel collar, which had been inserted into the soil the previous evening. The collars were all located on bare soil with no plants being enclosed within the collar or chamber system. The chamber was placed on the collar at approximately 8:00 a.m. and flushed with zero grade air for at least 1 h before data collection began at 9:00 a.m. This sampling scheme ensured that the concentrations within the chamber reached steady state prior to any data acquisition and allowed for the instruments to undergo their daily calibrations. Daily experiments ended at approximately 5:00 p.m. and the stainless steel collar was relocated to a random location within a 10 m radius of the mobile laboratory, in preparation for the next day's experiment. This procedure allowed a minimum of 16 h for any effect on soil NH_3 flux, due to soil disturbances caused by the insertion of the stainless steel collar, to dissipate.

2.2. Instrumentation

NH_3 concentrations were measured inside of the dynamic flow-through chamber system with a Thermo Environmental 17C Chemiluminescence NH_3 Analyzer (TECO 17C). The TECO 17C utilizes the following reaction in order to arrive at the NH_3 concentration:

$$NO + O_3 \rightarrow NO_2 + O_2 + h\upsilon. \tag{1}$$

Using a stainless steel converter heated to ~750°C, both the oxides of nitrogen (NO_x) and NH_3 ($N_T = NO_x + NH_3$) are converted to NO. NH_3 concentrations are obtained by subtracting the NO_x signal, which is obtained with a molybdenum converter heated to ~325°C, from the N_T signal (TECO, 1999). Calibrations of the instruments were conducted following protocols using a TECO 146 dilution/titration instrument in conjunction with a cylinder of 3.82 ppmV NO in N_2, 100 ppmV NH_3 in N_2 (National/Specialty gases) and zero grade air (National Welders). The TECO 146 was serviced and calibrated to specifications prior to each measurement campaign. A multipoint calibration was conducted prior to, and at the midpoint of the measurement period. Zero and span checks were conducted each day, according to the operator manuals.

2.3. Dynamic flow-through chamber

A dynamic flow-through chamber, lined with five-mil thick fluorinated ethylene propylene (FEP) Teflon, was used to measure NH_3 concentrations emitted from the soil. The translucent chamber, 26.5 cm in diameter, and 47.2 cm high (volume ~26 l), fits inside of a stainless steel collar, which is driven into the ground to a depth of ~10 cm (Fig. 2). Zero grade air, which is used as a carrier gas, is passed through the chamber at a constant flow rate (approximately 5 lpm), via a flow controller located on top of the chamber (Gilmont Shielded Industrial Flowmeter, accuracy ±5%). The air inside the chamber is mixed by a variable-speed, motor driven Teflon impeller. The sample exiting the chamber travels through Teflon tubing (0.64 cm outside diameter, 0.40 cm inside diameter) to the detection instruments. The entire measuring system, from the inlet port on the chamber to the point where the stream is analyzed in the instrument, is made of FEP Teflon to minimize chemical reactions with the sample stream. The NH_3 detection instruments draw 1.5 lpm, which resulted in a sample residence time in the Teflon lines (sample lines do not exceed 10 m) of approximately 5 s. The dynamic chamber system, with the continuous stirring provided by the impeller, meets the necessary criteria for performance as a continuously stirred tank reactor (CSTR). For performance as a CSTR, the chamber needs to be "ideally" mixed (Aneja, 1976). In ideal mixing, the composition of any elemental volume within the chamber is assumed to be the same as that of any other volume within the chamber. Trace experiments (residence time distribution) were used to test the flow and mixing characteristics of the system. The results of these mixing studies indicated that the dynamic chamber behaved as a "perfect" mixer with negligible stagnancy or channeling (Aneja et al., 2000). NH_3 fluxes were calculated using a mass balance approach as described in Roelle et al. (1999) and Aneja et al. (2000).

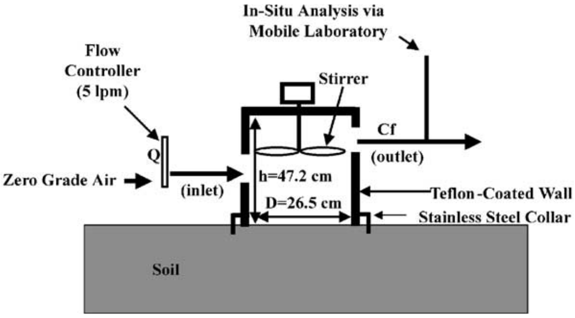

Fig. 2. Schematic of dynamic flow-through chamber system.

Utilizing the power law profile, which is frequently used in air pollution applications (Arya, 1999), we are able to estimate the wind velocities at a height of 0.1 m (the approximate height of the impeller above the soil–air interface), when the 10 m wind heights are known. The power law profile is given by

$$\frac{V}{V_r} = \left(\frac{Z}{Z_r}\right)^m, \tag{2}$$

where V_r is the wind velocity at a reference height Z_r and m is taken to be 0.1 for this smooth surface (Arya, 1988). Mean wind velocities were between 1 and 4 m s^{-1} (at a height of 10 m) throughout this measurement period. Using the power law profile (Eq. (2)), and the measured 10 m wind velocities, equates to wind speeds between 0.6 and 2.4 m s^{-1} at a height of 10 cm (approximate height of impeller). This calculated 10 cm wind speed approximates the wind speeds measured inside of the chamber (~ 1–$2.5\,\mathrm{m\,s^{-1}}$) using a hot wire anemometer.

2.4. Soil analysis

A soil sample was taken from the center of the chamber footprint at the end of each measurement period (1 sample per measurement period), and analyzed for soil pH, soil moisture and total Kjeldahl nitrogen (TKN = organic N + NH_3-N + NH_4^+-N) by the North Carolina State University Department of Biological and Agricultural Engineering. Percent water filled pore space (%WFPS) is a measure of soil water content and can be expressed as the percentage of pore spaces in the soil that are filled with water. The %WFPS is a convenient expression to describe soil moisture because it accounts for the differing bulk and particle densities of soils and therefore allows for the comparison of soil moisture from different soil types. Soil temperature was measured with a Campbell Scientific temperature probe (accuracy $\pm 3\%$) inserted into the soil to a depth of approximately 5 cm. Air temperatures (Campbell Scientific; accuracy $\pm 3\%$) were measured inside of a radiation shield at a height of 1.5 m. Soil data were stored in 15 min binned averages utilizing a Campbell Scientific 21 × Micrologger.

3. Results and discussion

3.1. Environmental controls on NH_3 flux

The ammonia–water and ammonia–soil system have been studied in the past because of their industrial importance and as a means for studying the absorption/desorption mechanism (Whitman and Davis, 1924; Godfrey, 1973; Levenspiel and Godfrey, 1974; Ibusuki and Aneja, 1984; Leuning et al., 1984; Warneck, 2000). These previous studies indicate that the three most important parameters in the biological and chemical processes which determine the NH_3 equilibrium and production rate are temperature, pH, and nitrogen content. In the soil environment these variables translate to soil temperature, soil pH, and the soil moisture and nitrogen content.

3.2. Soil temperature

The temperature dependence is linked to the NH_3 production/emission through chemical and biological processes occurring simultaneously in the soil environment. In the absence of recent N fertilization, ammonia appears in the soil through a process called mineralization or ammonification whereby microorganisms satisfy their energy needs in the soil by converting amino acids in the dead organic matter to NH_3 as in the following reaction (Delwiche, 1970; Kinzig and Socolow, 1994):

$$CH_2NH_2COOH + 11/2O_2 \rightarrow 2CO_2 + H_2O + NH_3. \quad (3)$$

Given that biochemical reactions have been shown to rise exponentially with temperature in the range between 288 and 308 K, one would expect there to be a corresponding increase in the soil NH_3 concentration as soil temperature increases (assuming that the system is not limited by soil organic matter content) (Warneck, 2000). In fact, this exponential dependence of both reduced and oxidized nitrogen trace species on soil temperature has been repeatedly demonstrated in both field and laboratory studies (Sherlock and Goh, 1985; Van der Molen et al., 1990; Roelle et al., 1999)

The NH_3 and NH_4^+ in the soil solution are in aqueous equilibrium:

$$NH_{4(aq)}^+ \rightleftharpoons NH_{3(aq)} \quad (4)$$

and if the NH_3 vapor pressure in solution is greater than the vapor pressure of NH_3 in the surrounding air than the NH_3 will be volatilized (Sherlock and Goh, 1985). This relationship can be expressed in the form of Henry's Law (H), where

$$H = (NH_{3(aq)})/(NH_{3(g)}) \quad (5)$$

and

$$\mathrm{Log}\,H = -1.69 + 1477.7/T \quad (6)$$

(Hales and Drewes, 1979; Sherlock and Goh, 1985).

From Eqs. (5) and (6), it can be shown that an increase in soil temperature will produce a corresponding increase of the $NH_{3(g)}$ concentrations in the soil. This same Henry's law equilibrium applies in water bodies (such as hog waste lagoons) and Aneja et al. (2001a) have developed a fundamental mechanistic ammonia model to predict lagoon NH_3 emissions based on this equilibrium. The Aneja et al. (2000) study confirmed that lagoon temperature was the dominant parameter affecting NH_3 emissions from lagoons and the temperature dependence model that they developed was then compared to a temperature dependence model developed in this study for NH_3 emissions from soil surfaces. Other physiochemical parameters that influence NH_3 emissions are pH, nitrogen content, and moisture content of the soil.

The calculated NH_3 fluxes (including rainfall totals which are discussed later) during the spring and winter 2000 measurement period can be seen in Fig. 3. The values calculated during this study fall within the range of NH_3 soil fluxes reported by other researchers (Table 3). The daily averaged NH_3 flux values plotted versus the daily averaged soil temperature (Fig. 4) reveal a statistically significant relationship ($p < 0.01$) with NH_3 flux increasing exponentially as soil temperature

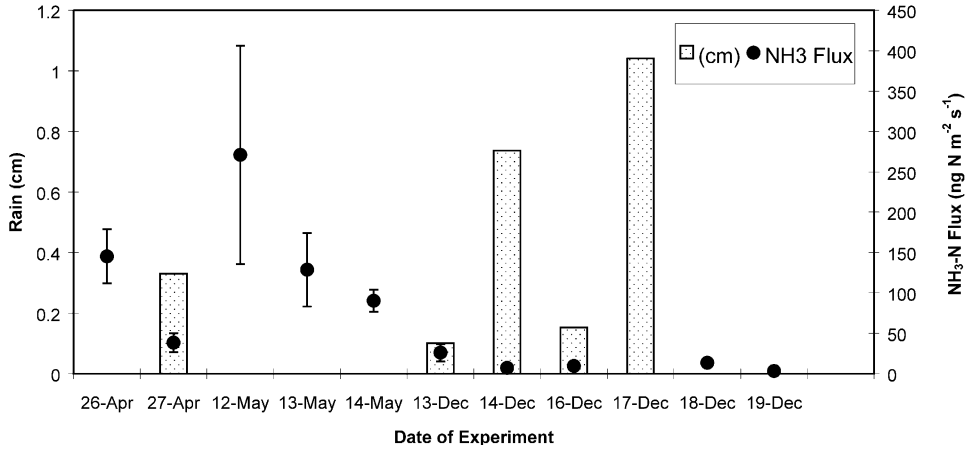

Fig. 3. Total rainfall (primary axis) and NH$_3$-N flux (secondary axis) versus day of experiment. Vertical bars represent one standard deviation of the ammonia flux.

Table 3
List of researchers and reported NH$_3$ flux values measured under various crop and fertilization scenarios

Researcher	Site description	Reported NH$_3$ flux values
Harrison et al. (1989)	Grass and crop surfaces	-20–100 ng N m^{-2} s^{-1}
Meixner et al. (1991)	Wheat	-12–25 ng N m^{-2} s^{-1}
Weber et al. (2000)	Post-fertilization (80 kg N ha^{-1}) winter wheat	
	1999	64 ng N m^{-2} s^{-1}
	2000	178 ng N m^{-2} s^{-1}
This study		
Spring	Corn crop, pre-fertilization	38–271 ng N m^{-2} s^{-1}
Winter	No crop planted	3–26 ng N m^{-2} s^{-1}
Aneja et al. (2000)	Anaerobic lagoon surface	
Spring		1706 ± 552 μg N m^{-2} min^{-1}
Summer		4017 ± 987 μg N m^{-2} min^{-1}
Fall		844 ± 401 μg N m^{-2} min^{-1}
Winter		305 ± 154 μg N m^{-2} min^{-1}

increases. The soil temperature model in this study [Log$_{10}$ NH$_3$-N Flux (ng N m^{-2} s^{-1}) = $0.054T_{\text{soil}} + 0.66$; $R^2 = 0.71$] and the lagoon temperature model in the Aneja et al. (2000) study [Log$_{10}$ NH$_3$-N Flux (μg N m^{-2} min^{-1}) = $0.048T_{\text{lagoon}} + 2.1$; $R^2 = 0.78$] were responsible for approximately the same amount of variability in the NH$_3$ flux from the soil and lagoon surfaces. This strong dependence of NH$_3$ emissions on temperature has been cited for other nitrogen (N) trace gases (NO, NO$_2$, and N$_2$O) with approximately the same results (Kim et al., 1994; Sullivan et al., 1996; Roelle et al., 1999). In fact, the US Environmental Protection Agency (EPA) currently utilizes this exponential temperature dependence in the biogenic emissions inventory system (BEIS) model to estimate the biogenic nitric oxide emissions (NO) which are then used as input data for ozone and air quality models (Birth and Geron, 1995; Thornton et al., 1997). The strong temperature dependence reported in this study suggests that a similar approach may also be effective in estimating the biogenic NH$_3$ emissions.

3.3. Soil pH, soil moisture, and soil nitrogen content

As previously discussed, other parameters such as soil pH and soil moisture have been identified as controlling NH$_3$ production. The [OH$^-$] produced as a result of the following dissociation in the soil solution

$$NH_{3(aq)} \leftrightarrow NH^{+}_{4(aq)} + OH^{-} \quad (7)$$

can be represented by

$$[OH^{-}] = K_w/[H^{+}] \quad (K_w = \text{water dissociation constant}). \quad (8)$$

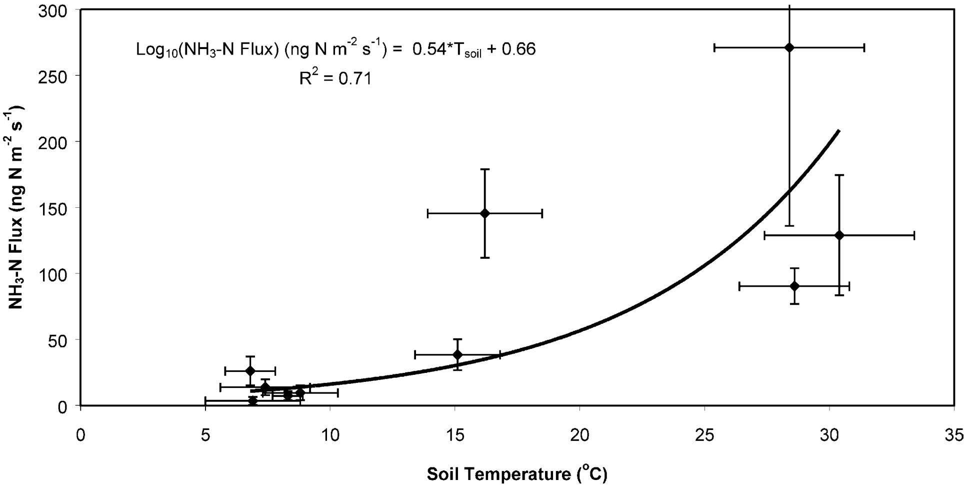

Fig. 4. Plot of NH_3-N flux versus soil temperature. Vertical lines represent one standard deviation of the average NH_3 flux, and horizontal bars represent one standard deviation of the temperature during that flux measurement period.

As the soil pH increases ($[OH^-]$ increases), the equilibrium is shifted towards more NH_3 being released (Warneck, 2000; Li, 2000), and studies have demonstrated pH to affect NH_3 emissions (Singh and Nye, 1988; Aneja et al., 2001b). However, in intensively managed agricultural soils, the pH value of a soil column (~20 cm) tends to remain fairly uniform (see Table 2), and therefore no significant relationships between soil pH and NH_3 flux can be discerned. The studies which identified soil pH as a significant variable typically looked at pH in the top 1–3 cm of the soil and were during fertilization events, both of which found much larger changes in pH values (1–3 pH units). Therefore it is recommended that future field studies should also include an analysis of soil pH over a few different sampling depths.

The soil moisture conditions at this field site are best described by Fig. 3, which shows the rain events in relation to the sampling days and measured flux values. The %WFPS (Table 2) also describes moisture conditions; however, the effect of our soil sampling technique (20 cm depth), has the potential to dilute the actual moisture content in the top few centimeters of the soil column, where the largest concentration of ammoniacal nitrogen has been shown to reside (Singh and Nye, 1986). As more water is introduced, pores in the soil matrix begin to fill and hinder the diffusion of NH_3 gas from the soil to the air (Kirk and Nye, 1991). Additionally, from an equilibrium standpoint, as the water content in the soil increases, the NH_3 decreases as the equilibrium moves towards the right hand side of Eq. (7). Increases in emissions have been observed when soils with high moisture content are subjected to drying via high winds or temperature. This increase or "pulse" is believed to be caused by the combination of an increase in the ammoniacal nitrogen concentration of the soil and greater diffusion through the relatively drier soil (Burch and Fox, 1989; Battye et al., 1994). A similar "pulse" in emissions (day 3 in Fig. 3) may be causing the large increase in emissions which occurred after the sharp decrease in soil moisture (decreased from 40.5%WFPS to 24.9%WFPS). While this observation is based on only one data point, prior to which there was a lapse of several days of data, it is supported by similar observations from other researchers (Burch and Fox, 1989; Battye et al., 1994).

The relationship of NH_3 volatilization and N content of the soil can be seen in Fig. 5. Several investigators have attempted to develop models describing the physical and chemical processes affecting the release of NH_3 from soil surfaces (Sherlock and Goh, 1985; Singh and Nye, 1986). Based on their mechanistic models, a linear dependence of NH_3 flux on soil nitrogen content was expected and found to explain more variability in the data than other attempted relationships. In both plots (a and b), there were relatively weak dependences of NH_3 flux on NH_3-N and TKN content of the soil ($R^2 = 0.12$ and 0.02 for NH_3-N and TKN respectively) when all data points are considered in the regression. Given the strong influence that soil moisture has on NH_3, both in terms of its equilibrium and in its control of diffusion through the soil, both NH_3-N and TKN were reanalyzed taking the moisture conditions into account. When 2 sampling days (rain events >0.3 cm and standing water evident in some parts of the field) were removed, there was an appreciable increase in the significance of N content on NH_3 release. The rain events which occurred on 13 and 16 December were both light mists with the majority of the total rainfall occurring after the sampling period. Interestingly, the

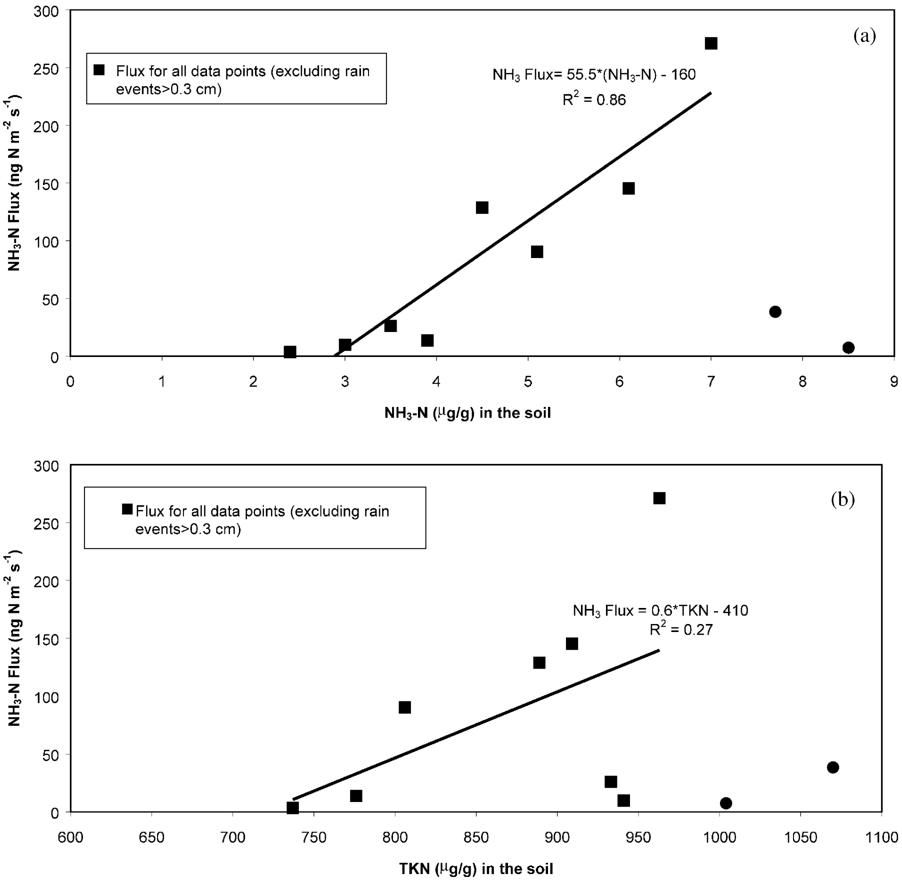

Fig. 5. Plot of NH_3-N flux versus nitrogen content of the soil: (a) NH_3-N (μg g^{-1}), (b) total Kjeldahl nitrogen (μg g^{-1}). Note that (■) represents the data points without rain events >0.3 cm and (●) represents those data points that were measured on days having rain >0.3 cm.

largest rainfall event (17 December) did not suppress NH_3 emissions on 18 December, relative to the other wintertime measurements. However strong winds associated with the frontal passage following the rainfall event did act to dry out the surface layer even though the soil core had the highest %WFPS. The greater dependence of NH_3 volatilization rates on NH_3 content ($R^2 = 0.86$) as compared to TKN ($R^2 = 0.27$) is expected as TKN is the sum of both ammoniacal N and organic N.

3.4. Budget for site

Aneja et al. (2000) described a temperature based model similar to the model described in this study, although the Aneja model related NH_3 emissions from hog waste lagoons to lagoon temperature. While the processes regulating NH_3 emissions from lagoon surfaces differ from those regulating soil NH_3 emissions, the temperature relationship is found to be applicable to both. The physical and chemical processes regulating the emissions from the lagoon and soil surfaces and their dependence on soil temperature are described in detail in Aneja et al. (2000) and Warneck (2000), respectively. Utilizing the temperature model developed in this study to estimate NH_3 emissions from soils and the temperature based algorithm developed by Aneja et al. (2000) to estimate NH_3 emissions from lagoons (see Table 3 for measured lagoon NH_3 emission averages), it is possible to estimate the relative seasonal source strengths of the soil and the lagoon.

Although this yearly estimate is based on a model developed from two seasons of data, the temperature dependence is assumed to remain consistent, during periods when the soil has not been recently fertilized, throughout diurnal cycles and throughout the year (Van der Molen et al., 1990; Aneja et al., 2000; Warneck, 2000). Using the daily averaged temperatures (information obtained from North Carolina State Climate Office), the seasonally averaged emissions from the

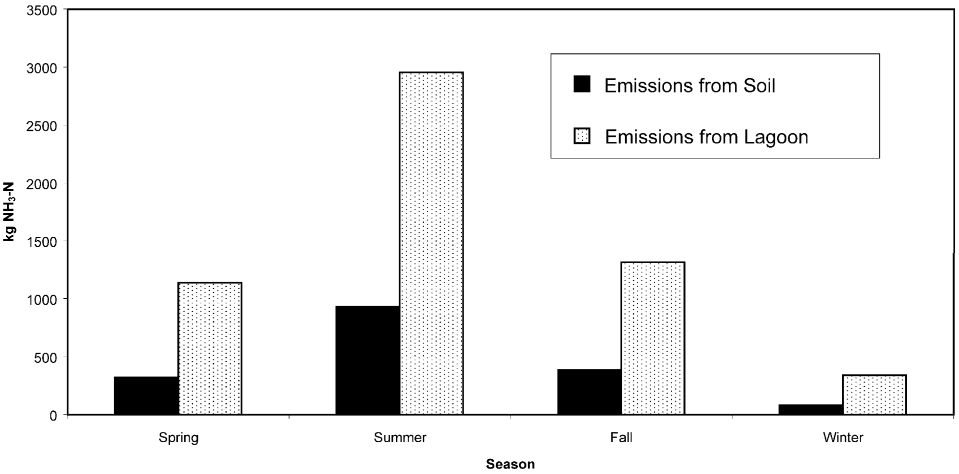

Fig. 6. Budget of NH_3-N estimates from soil and lagoon surfaces at the Upper Coastal Plain Research Site. Soil estimates were determined by applying the flux algorithm developed in this study to the total land area (~101 ha). Lagoon estimates were determined by applying the flux algorithm developed by Aneja et al. (2000) to the total lagoon surface area (~1 ha).

101 ha of soil surface at this site during spring, summer, fall, and winter were determined to be 324, 933, 383, and 83 kg NH_3-N respectively (Fig. 6). Similarly, the seasonally averaged lagoon emissions from the 1 ha of lagoon surface during spring, summer, fall, and winter were determined to be 1140, 2953, 1315, and 340 kg NH_3-N respectively. Therefore, the NH_3 emissions from soil surfaces represent approximately 28%, 32%, 29%, and 24% of the spring, summer, fall, and winter lagoon emissions. The typical practice in most hog operations is to spray the fields with the hog waste effluent instead of fertilizing them with commercially derived fertilizers. This field, however, was not sprayed and therefore this budget may be biased low, as emission factors for land spreading of slurry are often cited as being larger (~15–76%) than the factors for the commercially derived fertilizers (Misselbrook et al., 2000).

4. Conclusions

Utilizing a dynamic flow-through chamber technique, NH_3 flux values were calculated for the spring and winter (2000) at an upper coastal plain site in North Carolina. Soil pH remained relatively constant throughout the measurement period and therefore was not useful as an NH_3 flux predictor. The NH_3 flux values were most strongly correlated with soil temperature [$\text{Log}_{10}\,NH_3\text{-N Flux (ng N m}^{-2}\,\text{s}^{-1}) = 0.054T_{\text{soil}} + 0.66$; $R^2 = 0.71$], which may help to steer the way towards developing a temperature and land use type model (similar in design to the EPA's BEIS model for estimating biogenic NO emissions) to estimate biogenic NH_3 emissions. However, when the major rain events were eliminated, the role of soil nitrogen (both NH_3-N and TKN) in explaining the variability in NH_3 flux improved significantly.

The average NH_3 flux values from this study corresponded well with other reported values and confirmed that soils have smaller fluxes of NH_3 than lagoons (Table 3). However, as in most commercial animal operations the land area used for crops is significantly larger than the surface area for lagoons. A preliminary analysis revealed that given the relative sizes of the agricultural soils in comparison to the lagoons, the soils (soils represent ~28% of the lagoon NH_3 emissions) cannot be neglected when developing and apportioning NH_3 budgets. Further, the soil algorithm developed in this study was based on a crop which had not been fertilized for several months prior to the experimental period. Given that land spreading of slurry is estimated to release approximately 15–76% of the applied nitrogen may indicate that estimates presented in this study should be considered as a lower limit.

While temperature has often been shown to be a controlling variable in nitrogen trace gas emissions, other variables (pH, N-content, %WFPS) have displayed more mixed results (Williams et al., 1992; Matson et al., 1997). Therefore, future work should consist of field and laboratory studies to further investigate these relationships and data following slurry application should also be obtained to help refine the NH_3 budget for intensively managed agricultural soils. While this research does help to quantify the soil source strength, it does not shed much light on transport through canopies or on the effect ambient NH_3 concentrations have on deposition versus emissions. Even though the values reported in this study are within the range of other reported values, a side-by-side comparison of the differing NH_3 flux methodologies would be extremely beneficial in furthering our knowledge of this species.

Acknowledgements

We would like to express our sincere appreciation to the Division of Air Quality, North Carolina Department of Environment and Natural Resources (Contract No. EA 01001). The authors also wish to thank the North Carolina State University Air Quality Research Group for their technical discussions and assistance with data collection. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

References

Aneja, V.P., 1976. Dynamic studies of ammonia uptake by selected plant species under flow reactor conditions. Ph.D. Thesis, NC State University, Raleigh, NC, p. 216.

Aneja, V.P., Chauhan, J.P., Walker, J.T., 2000. Characterization of atmospheric ammonia emissions from swine waste storage and treatment lagoons. Journal of Geophysical Research 105, 11535–11545.

Aneja, V.P., Malik, B.P., Tong, Q., Kang, D., 2001a. Measurement and modeling of ammonia emissions at waste treatment lagoon–atmospheric interface. Water, Air and Soil Pollution, in press.

Aneja, V.P., Roelle, P.A., Murray, G.C., Southerland, J., Erisman, J.W., Fowler, D., Asman, W., Patni, N., 2001b. Atmospheric nitrogen compounds II: emissions, transport, transformation, deposition and assessment. Atmospheric Environment 35, 1903–1911.

Arya, S.P., 1988. Introduction to Micrometeorology. Academic Press, Inc., New York, NY, pp. 141–143.

Arya, S.P., 1999. Air Pollution Meteorology and Dispersion. Oxford University Press, New York, NY, pp. 98–100.

Asman, W.A.H., Cellier, P., Genermont, S., Hutchings, N.J., Sommer, S.G., 1998. Ammonia emission research: from emission factors to process descriptions. Eurotrac Newsletter 20, 2–10.

Battye, R.W., Overcash, C., Fudge, S., 1994. Development and selection of ammonia emission factors. EPA Contract Number 68-D3-0034, Work Assign. 0-3, USEPA, Research Triangle Park, North Carolina.

Birth, T.L., Geron, C.D., 1995. User's guide to the personal computer version of the biogenic emissions inventory system (PC-BEIS2), EPA-600/R-95-091, July.

Burch, J.A., Fox, R.H., 1989. The effect of temperature and initial soil moisture content on the volatilization of ammonia from surface applied urea. Soil Science 147, 311–318.

Delwiche, C.C., 1970. The nitrogen cycle. Scientific American 223, 137–146.

Dentener, F.J., Crutzen, P.J., 1994. A three-dimensional model of the global ammonia cycle. Journal of Atmospheric Chemistry 19, 331–369.

Godfrey, J.M., 1973. A new apparatus for studying mass transfer and reaction between two fluid phases. Ph.D. Thesis, Oregon State University, Corvallis, p. 154.

Hales, J.M., Drewes, D.R., 1979. Solubility of ammonia at low concentrations. Atmospheric Environment 13, 1133–1147.

Harrison, R.M., Rapsomanikis, S., Turnbull, A., 1989. Land-surface exchange in a chemically reactive system; surface fluxes of HNO_3, HCl and NH_3. Atmospheric Environment 23, 1795–1800.

Ibusuki, T., Aneja, V.P., 1984. Mass transfer of NH_3 into water at environmental concentrations. Chemical Engineering Science 39, 1143–1155.

Kim, D.-S., Aneja, V.P., Robarge, W.P., 1994. Characterization of nitrogen oxide fluxes from soil of a fallow field in the central piedmont of North Carolina. Atmospheric Environment 28, 1129–1137.

Kinzig, A.P., Socolow, R.H., 1994. Human impacts on the nitrogen cycle. Physics Today 47, 24–31.

Kirk, G.J.D., Nye, P.H., 1991. A model of ammonia volatilization from applied urea. V. The effects of steady-state drainage and evaporation. Journal of Soil Science 42, 103–113.

Lekkerkerk, L.J.A., Heij, G.J., Hootsmans, M.J.M., 1995. Dutch priority programme on acidification, ammonia: the facts. Secretariat Additional Programme on Acidification Research, Report No. 300-06, April.

Leuning, R., Denmead, O.T., Simpson, J.R., Freney, J.R., 1984. Processes of ammonia loss from shallow floodwater. Atmospheric Environment 18, 1583–1592.

Levenspiel, O., Godfrey, J.M., 1974. A gradientless contactor for experimental study of interface mass transfer with/without reaction. Chemical Engineering Science 29, 1723–1730.

Li, C.S., 2000. Modeling trace gas emissions from agricultural ecosystems. Nutrient Cycling in Agroecosystems 58, 259–276.

Matson, P., Firestone, M., Herman, D., Billow, T., Kiang, N., Benning, T., Burns, J., 1997. Agricultural systems in the San Juaquin Valley: development of emission estimates for nitrogen oxides. Technical Report, University of California, Berkeley, Contract No. 94-732.

Meixner, F.X., Böswald, F., Eilalmeier, K., Kramm, G., Ludwig, J., Müller, H., Nestlen, M., Terrey, B., Weber, P., 1991. Measurements of vertical fluxes of nitrogen compounds. In: EUROTRAC Annual Report, Part 4: BIATEX. EUROTRAC ISS, Fraunhofer Institute, Garmisch-Partenkirchen, pp. 60–66.

Misselbrook, T.H., Van Der Weerden, T.J., Pain, B.F., Jarvis, S.C., Chambers, B.J., Smith, K.A., Phillips, V.R., Demmers, T.G.M., 2000. Ammonia emission factors for UK agriculture. Atmospheric Environment 34, 871–880.

Roelle, P.A., Aneja, V.P., O'Connor, J., Robarge, W.P., Kim, D.-S., Levine, J.S., 1999. Measurement of nitrogen oxide emissions from an agricultural soil with a dynamic chamber system. Journal of Geophysical Research 104, 1609–1619.

Schlesinger, W.H., Hartley, A.E., 1992. A global budget for atmospheric NH_3. Biogeochemistry 15, 191–211.

Sherlock, R.R., Goh, K.M., 1985. Dynamics of ammonia volatilization from simulated urine patches and aqueous urea applied to pasture. II. Theoretical derivation of a simplified model. Fertilizer Research 6, 3–22.

Singh, R., Nye, P.H., 1986. A model of ammonia volatilization from applied urea. I. Development of the model. Journal of Soil Science 37, 9–20.

Singh, R., Nye, P.H., 1988. A model of ammonia volatilization from applied urea. IV. Effect of method of urea application. Journal of Soil Science 39, 9–14.

Sullivan, L.J., Moore, T.C., Aneja, V.P., Robarge, W.P., 1996. Environmental variables controlling nitric oxide emissions from agricultural soils in the southeast United States. Atmospheric Environment 30, 3573–3582.

Sutton, M.A., Pitcairn, C.E.R., Fowler, D., 1993. The exchange of ammonia between the atmosphere and plant communities. In: Begon, M., Fitter, A.H. (Eds.), Advances in Ecological Research, Academic Press: New York, Vol. 24, pp. 301–390.

Thermo Environmental Instruments Inc., 1999. Model 17C Chemiluminescence NH_3 Analyzer Instruction Manual, Franklin, MA.

Thornton, F.C., Pier, P.A., Valente, R.J., 1997. No emissions from soils in the southeastern united states. Journal of Geophysical Research 102, 21189–21195.

Van der Molen, J., Beljaars, A.C.M., Chardon, W.J., Jury, W.A., Van Faassen, H.G., 1990. Ammonia volatilization from arable land after application of cattle slurry. 2. Derivation of a transfer model. Netherlands Journal of Agricultural Science 38, 239–254.

Warneck, P., 1988. Chemistry of the Natural Atmosphere. Academic Press, Inc., New York, NY, pp. 422–425.

Warneck, P., 2000. Chemistry of the Natural Atmosphere, 2nd Edition. Academic Press, Inc., New York, NY, pp. 511–517.

Weber, A., Gutser, R., Schmidhalter, U., 2000. Results from field experiments on ammonia losses after urea application with regard to measurement methodologies. In: Menzi, H. (Ed.), Proceedings of UN/ECE Ammonia Expert Group. Swiss College of Agriculture, Berne, pp. 18–20.

Whitman, W.G., Davis, D.S., 1924. Comparative absorption rates for various gases. Industrial Engineering Chemistry 16, 1233–1237.

Williams, E., Guenther, A., Fehsenfeld, F., 1992. An inventory of nitric oxide emissions from the soil in the United States. Journal of Geophysical Research 97, 7511–7519.