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Measurement and analysis of atmospheric ammonia emissions from anaerobic lagoons

V.P. Aneja*, B. Bunton, J.T. Walker[1], B.P Malik

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

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Abstract

Ammonia-nitrogen flux (NH_3-N = (14/17)NH_3) was determined from six anaerobic swine waste storage and treatment lagoons (primary, secondary, and tertiary) using the dynamic chamber system. Measurements occurred during the fall of 1998 through the early spring of 1999, and each lagoon was examined for approximately one week. Analysis of flux variation was made with respect to lagoon surface water temperature ($\sim$15 cm below the surface), lagoon water pH, total aqueous phase $NH_x(= NH_3 + NH_4^+)$ concentration, and total Kjeldahl nitrogen (TKN). Average lagoon temperatures (across all six lagoons) ranged from approximately 10.3 to 23.3°C. The pH ranged in value from 6.8 to 8.1. Aqueous NH_x concentration ranged from 37 to 909 mg N l^{-1}, and TKN varied from 87 to 950 mg N l^{-1}. Fluxes were the largest at the primary lagoon in Kenansville, NC (March 1999) with an average value of 120.3 μg N m^{-2} min^{-1}, and smallest at the tertiary lagoon in Rocky Mount, NC (November 1998) at 40.7 μg N m^{-2} min^{-1}. Emission rates were found to be correlated with both surface lagoon water temperature and aqueous NH_x concentration. The NH_3-N flux may be modeled as ln(NH_3-N flux) = 1.0788 + 0.0406T_L + 0.0015([NH_x]) ($R^2 = 0.74$), where NH_3-N flux is the ammonia flux from the lagoon surface in μg N m^{-2} min^{-1}, T_L is the lagoon surface water temperature in °C, and [NH_x] is the total ammonia-nitrogen concentration in mg N l^{-1}. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

1.1. Background

Atmospheric ammonia (NH_3) is a very important constituent of the environment because it is the dominant gaseous base specie present in the atmosphere. Its properties, including water solubility, make NH_3 important in atmospheric chemistry and physics. Ammonia is known to affect ecosystems at relatively low concentrations (Genfa et al., 1998). Once released into the atmosphere, NH_3 has a lifetime of less than 1 day to 5 days (Warneck, 1988). It will, therefore, most likely deposit to the Earth's surface close to its source. When airborne, NH_3 reacts with acidic species such as sulfuric acid (H_2SO_4), nitric acid (HNO_3), and hydrochloric acid (HCl) to form ammonium sulfate, ammonium nitrate, or ammonium chloride, respectively. Approximately 10% of atmospheric NH_3 is oxidized by the hydroxyl radical (OH) to form an amide radical (Finlayson-Pitts and Pitts, 1996). Ammonia may also be removed from the atmosphere by wet and dry deposition processes. Once transformed into ammonium (NH_4^+) aerosol, the lifetime of the species increases (ranging from 1 to 15 days) (Aneja et al., 1998b) as its dry deposition velocity decreases. Thus, NH_4^+ aerosol can be transported over larger distances downwind of sources than NH_3. The rate of conversion of NH_3 to NH_4^+ is largely unknown, but it is expected to have an important bearing on the spatial scale of NH_3 deposition from individual sources. The reaction rates depend mostly on the acid concentration,

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

[1] Present address: US EPA, National Risk Management Research Laboratory Research Triangle Park, NC 27711, USA.

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

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humidity, and temperature of the air (Seinfeld and Pandis, 1998).

Environmental consequences associated with atmospheric NH_3 and its deposition include eutrophication, soil acidification, and aerosol formation. In the vicinity of sources, direct absorption into some plants through needles and leaves may impact vegetation. It is believed that atmospheric deposition is a significant source of nitrogen to coastal waters (Pearl and Whitall, 1999). The US Atlantic coast is subject to many environmental hazards associated with excess nitrogen, including growing frequencies of toxic and non-toxic phytoplankton blooms, associated hypoxia and anoxia, fish kills, and general declines in fisheries of desirable "clean water" species (Pearl, 1995). Also, an increase in the frequency of toxic "red tide" dinoflagellate blooms is due at least in part from increased nitrogen deposition (Pearl, 1995). In North Carolina, nutrient loading has impacted coastal river systems, such as the Neuse River Basin, for several years (Aneja et al., 1998a). Approximately 35–60% of the total nitrogen loading to North Carolina coastal waters is thought to be associated with atmospheric deposition (Pearl et al., 1999).

1.2. Ammonia emissions

The largest contributor of ammonia to the global budget is domestic animal waste, with emission estimates ranging from 20 to 35 $Tg\,N\,yr^{-1}$ (Bouwman et al., 1997; Warneck, 1988). Other major global sources include emissions from soils, volatilization losses from fertilizers, and biomass burning. Although an important contributor to the atmospheric nitrogen budget, NH_3 sources and emission strengths have until recently received little attention in the US. In North Carolina, domestic animal waste is the leading contributor of atmospheric NH_3, as indicated by Table 1. With an estimated 68,540 tons of ammonia emitted per year, swine leads all other domesticated animals in North Carolina NH_3 emission (Aneja et al., 1998a). This is about 47% of the total NH_3 emissions for the state, and accounts for ~20% of North Carolina's nitrogen budget.

During the last decade, North Carolina has observed drastic growth in the hog industry. Since 1990, the statewide hog population has increased from about 2.5 to almost 10 million (NCDA, 1999). Most of this growth has been focussed on the coastal plain region of the state, where more than 8.5 million hogs now reside (Walker, 1998; Aneja et al., 2000; Walker et al., 2000a,b). Walker (1998) and Walker et al. (2000a), through the use of source-receptor modeling have shown that under specific meteorological conditions NH_3 emissions from certain areas within the Coastal Plain region enhance wet deposition of NH_4^+/NH_3 at National Atmospheric Deposition Program/National Trend Network (NADP/NTN) sites up to ~80 km away. Several sensitive coastal and estuarine

Table 1
Sources and estimates of nitrogen emissions for North Carolina. Adapted from Aneja et al., 1998b

Source[a]	Nitrogen species Emitted per year[b]	Estimated tons of N Emitted per year[c]	% of Total N[d]
Highway mobile (1990)	NO_x	78,509	23.7
Point sources (1994)	NO_x	77,798	23.6
Area and non-road mobile	NO_x	24,452	7.4
Biogenic NO_x (1995)	NO_x	9926	3.0
Swine (1995)	NH_3	68,540	20.6
Cattle (1995)	NH_3	24,952	7.5
Broilers (1995)	NH_3	13,669	4.1
Turkeys (1995)	NH_3	16,486	5.0
Fertilizer application (1999)	NH_3	8270	2.5
"Other" chickens (1995)	NH_3	6476	2.0
NH_3 point sources	NH_3	1665	0.5
Total		330,743	100.0

[a] Nitrogen calculated from NO_x emissions assumes 100% NO_2 although the actual proportion is closer to 95%. Thus, NO_x-N (tons) ×(14/46); and NH_3-N (tons) = NH_3 (tons)×(14/17).

[b] NO_x emission taken from DAQ inventories developed for modeling purposes; NH_3 emissions based upon factors presented in Battye et al. (1994), and production statistics from the NCDA.

[c] Two minor ammonia sources, together totaling < 6000 tons statewide, have been omitted. Factors for these, emissions from sewage treatment plants and emissions associated with human breathing, are based upon very limited data and are currently being reevaluated.

[d] Relative proportions of NO_x ~58%, NH_x ~42%.

ecosystems are within this 80 km region, and therefore could be impacted by NH_3 originating from the coastal plain region. The eutrophication of these ecosystems, along with soil acidification, particle formation, and odor, are the primary reasons why accurate emission factors for NH_3 sources, along with measurement-based estimates of wet atmospheric deposition and dry deposition to various surface types, are needed. Quantifying NH_3 emissions from swine operations is crucial in determining the fraction of NH_4^+ and NH_3 entering natural environments via the atmosphere.

The primary objective of this study was to measure NH_3 flux from a variety of anaerobic waste storage and treatment lagoons (primary, secondary and tertiary) using a dynamic chamber system, at various types of hog facilities (both commercial and research) around the state of North Carolina, extending the work of Aneja et al. (2000a). These include two research scale farms and two commercial operations. At these locations measurements were made on primary, secondary and/or tertiary lagoons. However, both the pH of the commercial primary waste storage and treatment lagoons and the animal population in the present study are lower than that in Aneja et al. (2000a). Emphasis was placed on quantifying lagoon emissions and illustrating seasonal emissions variability. The secondary objective was to parameterize the NH_3 flux process with respect to changes in physicochemical parameters (lagoon temperature, pH, and aqueous $[NH_x]$).

2. Materials and methods

2.1. Sampling sites

Fluxes of ammonia were determined at four different locations within the state of North Carolina. Table 2 lists summary of NH_3 flux statistics, site locations, sampling periods, and the lagoon surface areas. All lagoons sampled were anaerobic, meaning the bacteria used for the treatment of organic wastes were not dependent on dissolved oxygen in the lagoon. The first farm (Raleigh, NC, Research Farm) (15–23 September and 6–17 October, 1998) housed close to 1800 animals. Six to eight barns contained hogs that were in their farrowing, nursery, breeding, finishing, and gestation periods. The farm contained both a primary and a secondary lagoon. Waste from all the hog sheds (urine and feces) was flushed out with recycled lagoon water and discharged into the primary lagoon from the top (top loading). The secondary lagoon was connected to the primary by a pipe. Flux of NH_3 was determined from both lagoons. The second operation (Rocky Mount, NC Research Farm) (5–15 and 19–25 November, 1998), located in Edgecombe County near Rocky Mount, contained around 1450 animals, ranging in size from nursery piglets to large sows. Two barns top loaded waste into a primary lagoon and five barns emptied directly into a second primary lagoon, with a tertiary lagoon adjacent to and connected via piping to the second primary lagoon. Fluxes were determined from both the second primary and tertiary lagoons. The second primary lagoon was loaded via flushing and pit recharge methods. Located in Duplin County near Kenansville, the third farm sampled (28 February–9 March, 1999) was a commercial operation with approximately 4400 finishing animals. Four barns supplied a slightly larger lagoon with waste by the flushing method, and a slightly smaller lagoon was top loaded with waste from two pit recharge barns. Flux was measured from only the smaller of the two lagoons, but both had similar aqueous NH_x concentrations based on initial samples taken from each lagoon. The fourth operation from which flux was determined (19–27 March, 1999) is

Table 2
Summary of average daily NH_3-N[a] fluxes

Lagoon site and sample dates	Lagoon surface area[b]	Mean[c]	Minimum[c]	Maximum[c]
15–23 September 1998 Raleigh, NC, research farm (primary)	7806.7	80.11	39.72	243.13
6–17 October 1998 Raleigh, NC, research farm (secondary)	3325.9	57.76	17.03	129.75
5–15 November 1998 Rocky Mount, NC, research farm (tertiary)	1214.1	40.74	22.38	84.37
19–25 November 1998 Rocky Mount, NC, research farm (second primary)	3642.3	51.49	31.89	119.84
28 February–9 March 1999 Kenansville, NC, commercial farm (primary)	4905.3	120.31	49.76	374.14
19–27 March 1999 Warsaw, NC, commercial farm (primary)	3876.1	107.58	57.20	204.68

[a] NH_3-N flux = (14/17) NH_3 flux.
[b] Unit of surface area is m^2.
[c] Units of daily flux are ug N m^{-2} min^{-1}.

also located in Duplin County, near Warsaw, NC. This commercial operation contained four barns that accommodated a total of 2500 finishing animals. Four buildings emptied waste directly into one primary lagoon via the flush system.

2.2. Slurry composition and analysis

Lagoon water samples were taken on most days during the flux measurement periods and submitted to the Department of Biological and Agricultural Engineering (BAE), North Carolina State University, to be analyzed for the concentration of total ammonia nitrogen ($[NH_x] = [NH_3\text{-N}] + [NH_4^+\text{-N}]$) in the slurry and determination of total Kjeldahl nitrogen (TKN). TKN is the sum of the organic nitrogen and total ammonia-nitrogen ($\text{TKN} = \text{Organic N} + (NH_3\text{-N}) + (NH_4^+\text{-N})$). The BAE Environmental Analysis Laboratory uses an ammonia–salicylate method for automated analysis of NH_x concentration, and a persulfate digestion and ammonia–salicylate method for automated analysis of TKN, similar to that found in US. EPA manual 351.2 (1979) with some slight modifications including dialysis.

2.3. Flux measurements

Ammonia flux was determined using a dynamic chamber system with continuous impeller stirring (~ 100 rpm) (Aneja et al., 2000a, 1996; Chauhan, 1999; Kim et al., 1994; Kaplan et al., 1988). Early fall measurements were made from 15 to 23 September 1998. Fall measurements continued during the following periods; 6–17 October 1998, 5–15 November 1998, and 19–25 November 1998. Winter measurements occurred from 28 February to 9 March 1999. 19–27 March 1999 encompasses the Spring measurement period. Measurements were halted during precipitation events. Lagoon water temperature was continually monitored using a Fascinating Electronics temperature probe (Model # LM334Z) located 15 cm below the lagoon surface about 48 cm from the chamber. Continuous pH measurements were made, adjacent to the temperature probe, using a Cole–Parmer double junction submersible electrode (Model # P-05993-81).

2.4. Flux calculation

Fig. 1 illustrates the chamber/platform sampling system. A 1.22 m × 1.22 m floating platform is used to hold the chamber system above the water. A hole is cut in the center of the platform in which the chamber rests, allowing the bottom of the chamber to penetrate the lagoon surface by 3–4 cm, thus forming a seal between the lagoon surface and the air within the chamber.

The following mass balance equation is used when calculating the flux of a particular species C from the measured concentration of C in the chamber:

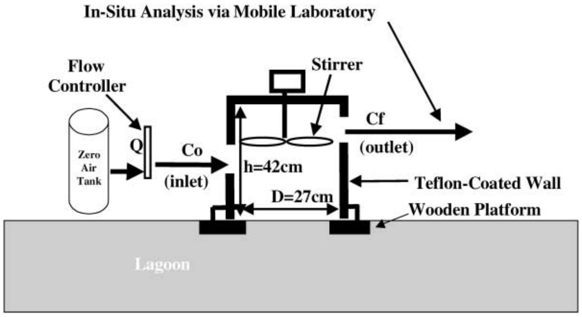

Fig. 1. Schematic of the floating dynamic flow-through chamber system.

$$\frac{d[C]}{dt} = \left[\frac{Q[C_0]}{V} + \frac{JA_L}{V}\right] - \left[\frac{LA_c[C]}{V} + \frac{Q[C]}{V}\right] - R \quad (1)$$

where C is the concentration of species C in the chamber, Q the flow rate of the carrier gas through the chamber, C_0 the concentration of C in ambient air, V the volume of the chamber, J the emission flux, A_L the lagoon surface area covered by the chamber, A_C the inner surface area of the chamber, L the loss term by the chamber wall per unit area assumed first order in $[C]$, R the chemical production rate in the chamber and h the internal height of the chamber.

When using zero air as a carrier gas, $C_0 = 0$, and Eq. (1) is simplified to

$$\frac{dC}{dt} = \frac{J}{h} - \left[\frac{L}{h} + \frac{Q}{V}\right][C]. \quad (2)$$

Zero-grade air is pumped in at a constant rate, but these rates often varied from site to site, within the range of $0.87\,\text{l}\,\text{min}^{-1}$ and $3.42\,\text{l}\,\text{min}^{-1}$. The air inside the chamber is continually mixed by an electric Teflon impeller (20 cm diameter at 100 rpm).

To determine the steady-state concentration (C) in the chamber, air is initially drawn through a Stainless Steel Measurement Technologies 1000 N NH_3 converter, operating at 800°C, which converts NH_3 and NO_y(NO_x + all reactive odd nitrogen species) in the sample into nitric oxide (NO). This concentration of NO is then determined via the standard chemiluminescence technique using an Advanced Pollution Instrumentation (API) Model 200 analyzer. A portion of the sample is also passed through a molybdenum converter which converts only the NO_y to NO. The difference between the ($NH_3 + NO_y$) and (NO_y) signals gives the NH_3 concentration in the chamber. The API is calibrated daily using a ThermoEnvironmental Instruments Model 146 Dynamic GasCalibration System, along with zero air and a known concentration of NO. The efficiency of the high-temperature converter is calculated by introducing a known concentration of NH_3.

The loss term L in Eq. (2) can be determined empirically by using a method developed by Kaplan et al. (1988). One plots the value of $-\ln(C_{ss} - C)/(C_{ss} - C_0)$ versus time (t), where C_{ss} is the concentration in the chamber after the flow rate is reduced and allowed to reach a second steady state, C is the concentration at any time (t) after the flow rate is reduced, and C_0 is the equilibrium concentration in the chamber when it reaches the steady state at an initial flow rate. From the above plot, one determines the slope of the best-fit line, which is equal to $(L/h + Q/V)$, and from which L is determined. Once L is known, J is obtained at steady state from the following:

$$\frac{J}{h} = \left[\frac{L}{h} + \frac{Q}{V}\right][C]. \tag{3}$$

For this study, the calculated value for the wall loss term L was $0.046\,\mathrm{cm\,s^{-1}}$.

3. Results and discussion

3.1. Dynamic chamber system gas flow characteristics

The ammonia–water system has been studied in the past because of its industrial importance and as a means for studying the absorption/desorption mechanism (Whitman and Davis, 1924; Godfrey, 1973; Levenspiel and Godfey, 1974; Ibusuki and Aneja, 1984; Leuning et al., 1984). All these previous studies indicate that generally both the gas- and liquid-phase resistance are equally important in determining the overall desorption/absorption rate.

The measurements described for determining ammonia flux at the lagoon-atmosphere interface are made with the dynamic chamber system with continuous impeller stirring (the carrier gas flow rate through the chamber and stirrer speed may be changed). Utilizing the power-law profile which is frequently used in air pollution applications (Arya, 1999), we are able to estimate wind velocities at a height of 0.1 m (the height of the impeller above water–air interface) when wind speeds at 10 m height is known i.e. measured the power-law profile is given by

$$\frac{v}{v_r} = \left(\frac{Z}{Z_r}\right)^m, \tag{4}$$

where v_r is the wind velocity at a reference height Z_r and m is taken to be 0.1 for water surfaces (Arya, 1988).

During this study, mean wind velocities were between 1 and $4\,\mathrm{m\,s^{-1}}$ at a height of 10 m. Through the power-law profile above, this equates to wind speeds between 0.6 and $2.4\,\mathrm{m\,s^{-1}}$ at a height of 10 cm which is similar to wind speeds inside the chamber (measured with a hot wire anemometer between ~ 1 and $2.5\,\mathrm{m\,s^{-1}}$) for our design configuration.

The dynamic chamber system with continuous impeller stirring 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 the same as that of any other volume. Tracer experiments (Residence Time Distribution) were used to test the flow and mixing characteristics of the system. The results of these mixing studies showed that the dynamic chamber behaved as a "perfect" mixer with negligible stagnancy or channeling.

Recently, a study was conducted by the authors on the dynamic chamber technique to explore possible differences between the air temperature inside the chamber and the ambient air temperature. The study was conducted during 12–14 May, 1999, at the primary lagoon sampled in Raleigh. On 12 May, both air inside the chamber and ambient air ranged from 15 to 34°C, with an average daily temperature difference of 2.47°C. On 13 May, both air inside the chamber and ambient air ranged from 18 to 36°C, with an average daily temperature difference of 3.37°C.

3.2. Lagoon temperature and ammonia flux

Ammonia fluxes were determined continuously on each of six lagoons in order to develop a 24 h profile of NH_3-N flux variation. Fig. 2 shows that there is a daytime maximum that occurs between 3:00 and 5:00 p.m. usually the warmest times of the day. Several previous studies on animal waste have also found temperature to be a strong factor in controlling the release of NH_3 into the atmosphere (Aneja et al., 2000a; Chauhan, 1999; Sommer, 1997; Dewes, 1996; Aarnink et al., 1995; Sommer et al., 1991; Muck and Steenhuis, 1982). Fig. 3 shows the diurnal profile of ammonia flux and lagoon surface water temperature for each lagoon separately. Although various parameters such as $[NH_x]$ and pH varied from lagoon to lagoon (Table 3), it is still possible to evaluate the differences in the daily trend of NH_3 flux from each lagoon, as demonstrated. Here, each hourly data point for a particular lagoon represents an average of hourly NH_3 flux values over the number of observation days. Although NH_3 flux magnitudes vary across lagoons, they have similar diurnal structure. The results of this study show that the temperature effect on NH_3 flux is common across different lagoons, which supports the findings of Aneja et al. (2000a).

During this study, measurements were not extended through the more extreme winter and summer seasons. Although hourly lagoon temperatures ranged from 1.9 to 29.9°C, the average temperatures for the various observation periods fell within the range of 10.3 to 23.3°C, as

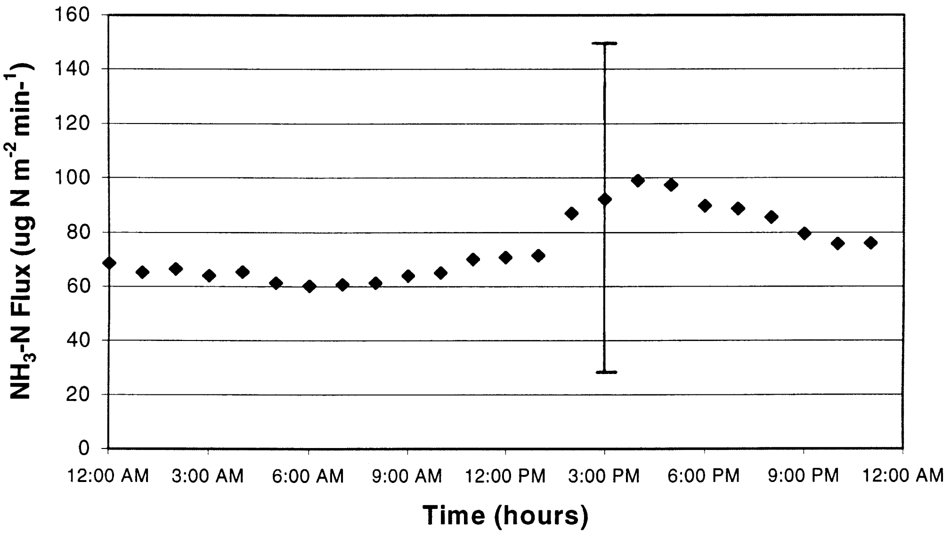

Fig. 2. Diurnal variation of the composite hourly average ammonia-nitrogen flux values (from all six lagoons combined).

shown in Table 3. This allowed the relationship between lagoon temperature and NH_3-N flux to be examined only across a some what small range of temperatures. Daily measurements generated 144 values of flux ($6\,h^{-1}$), and 24 values of temperature (continuous measurement averaged into 1 h blocks). Regression analysis shows a statistically significant ($p < 0.10$) positive correlation between flux and lagoon temperature at all sites. This does not include the second primary lagoon at Rocky Mount, where there were no corresponding hourly flux and temperature values. The percent variation in flux accounted for by variation in lagoon temperature averaged approximately 45% across individual sites and ranged from approximately 26% at the Raleigh secondary lagoon to 60% at the Rocky Mount tertiary lagoon. To further illustrate this temperature effect, daily averaged values for temperature and NH_3-N flux were analyzed. These are further separated into observation periods with average lagoon temperatures smaller or larger than 15°C. Fig. 4 shows an exponential ($r^2 = 0.45$) relationship between lagoon surface water temperature and NH_3-N flux. Since the mass transfer coefficients of NH_3 in water are exponential functions of temperature in the range of 5–30°C (Ibusuki and Aneja, 1984), this may be expected. Another study on a commercial hog waste lagoon (Aneja et al., 2000a) with greater than 10,000 hogs found a stronger relationship ($r^2 = 0.76$) between the two parameters. A possible reason for this difference is that this study has examined NH_3 emissions from six lagoons (four research scale and two small (<4500 hogs) commercial operations), whereas the earlier study examined only one large commercial lagoon with a higher lagoon pH. The behavior of the smaller size lagoons may not necessarily be identical to that of their larger counterparts. It is also possible that some physicochemical parameters play different roles depending on the type of lagoon and the season of the year. Another reason for the discrepancy is that no summer measurements were taken in this study. It was found that the percent of total yearly NH_3 emission attributable to summer months at one site is near 60% (Aneja et al., 2000a). During the summer, the production of NH_3 from the decomposition of urine and feces in the lagoon increases due to the higher seasonal temperatures. These higher temperatures also cause more NH_3 to volatilize from the surface of the lagoon.

3.3. Lagoon pH and ammonia flux

Lagoon pH plays a role in the potential for ammonia volatilization. The pH values observed in the various lagoons fell within a range of 6.8–8.1 (Table 3). In a lagoon, $[NH_3]$ will be in solution with $[NH_4^+]$ according to the following equilibrium reaction (Warneck, 1988):

$$NH_3(aq) + H_2O(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq). \quad (5)$$

The pH controls the direction of equilibrium in Eq. (5). Increasing the pH implies that the concentration of the hydroxyl ion ($[OH^-]$) increases, thereby shifting the equilibrium to the left, and subsequently more ammonia is liberated. Likewise, increasing the water content of the lagoon, e.g. precipitation events, shifts the equilibrium

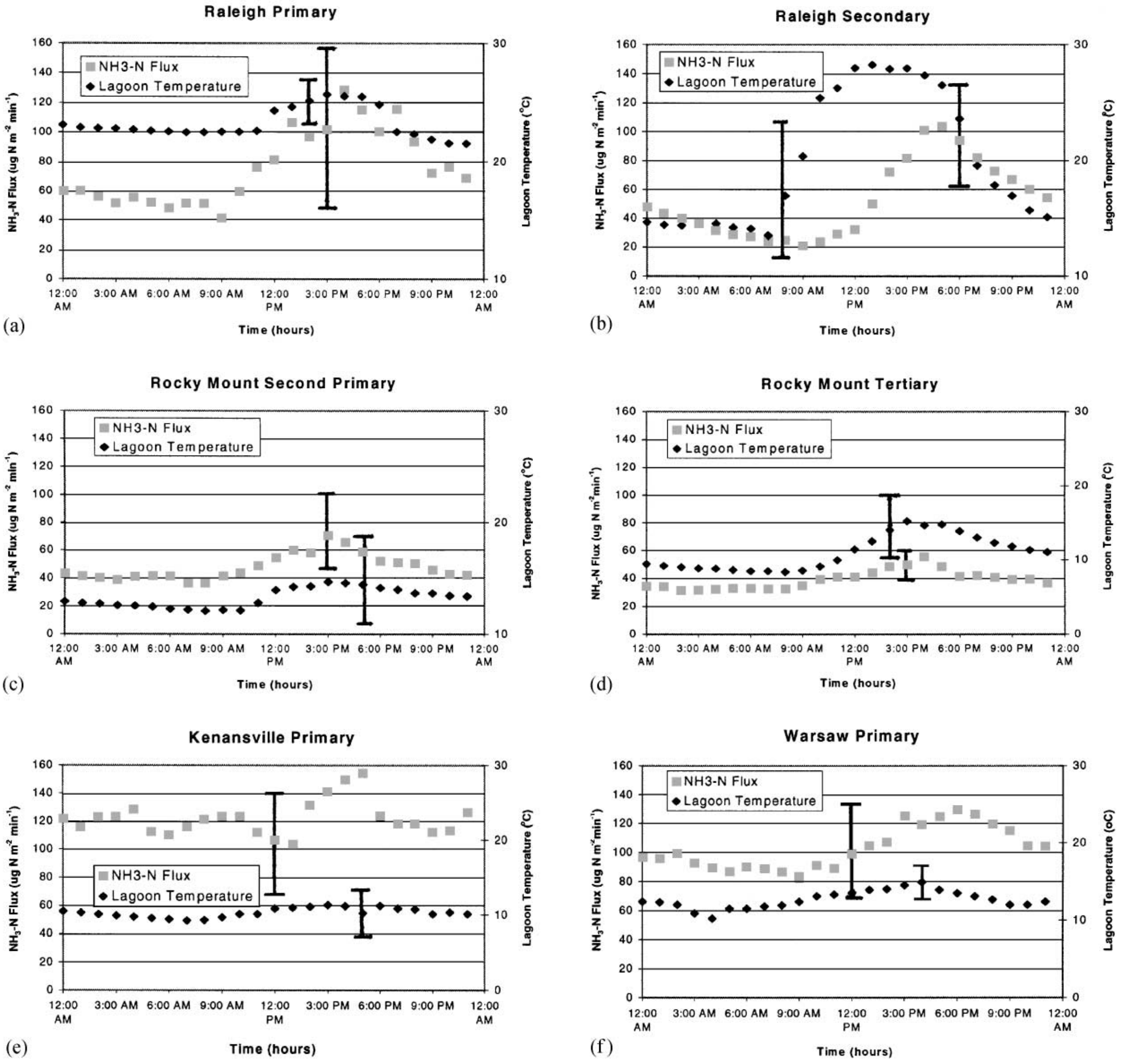

Fig. 3. (a)–(f). Diurnal ammonia-nitrogen flux and lagoon surface water temperature at individual sites.

slightly towards the right, causing the ammonia to be more tightly bound in solution. Several published modeling studies (Aneja et al., 2000b; Muck and Steenhuis, 1982; Olesen and Sommer 1993; Sommer et al., 1991) corroborate this positive relationship between NH_3 flux and pH.

As NH_4^+ dissociates, it releases a hydrogen ion (H^+) as shown in Eq. (6).

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq). \qquad (6)$$

When ammonia loss occurs, there should be proton acceptors in the solution, according to Eq. (6). Bicarbonate ions, which are formed as a product of the hydrolysis of urea and microbial conversion of organic matter, most commonly acquiesce to the surplus hydrogen ions, as shown in Eq. (7) (Sommer et al., 1991):

$$CO_2(aq) + H_2O(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq). \qquad (7)$$

The pH of the waste slurry is expected to undergo several changes. When fresh waste slurry is added to a lagoon, it has higher concentrations of total inorganic carbon than of NH_4^+ and NH_3 (Olesen and Sommer, 1993). Since the water solubility of carbon dioxide is 200

Table 3
Summary of the mean and range of various lagoon physico-chemical parameters by sampling period and location

Lagoon site and sample dates	Lagoon temperature[a]	Lagoon pH	$[NH_x]$[b]	TKN[b]
15–23 September 1998	23.3	7.78	104.8	185.7
Raleigh NC (primary)	21.4–28.9	7.0–8.1	101–110	146–202
6–17 October 1998	20.1	6.94	41.5	86.8
Raleigh NC (secondary)	7.5–29.9	6.8–7.3	37–44	82–93
5–15 November 1998	12.0	7.41	298.8	512.2
Rocky mount NC (tertiary)	1.9–16.9	6.8–8.0	288–311	497–530
19–25 November 1998	12.5	7.04	350	569
Rocky mount NC (second primary)	11.2–14.1	6.8–7.4	350	569
28 February–9 Mar 1999	10.3	7.33	550.0	677.8
Kenansville NC (primary)	8.1–14.4	6.8–8.1	543–560	672–686
19–27 March 1999	17.8	6.82	786.8	1387.8
Warsaw NC (primary)	13.3–23.5	6.8–7.1	709–909	881–2102

[a] Units of lagoon temperature are °C.
[b] Units of $[NH_x]$ and TKN are $mg\,N\,l^{-1}$.

times lower than the solubility of ammonia, pH will increase initially as more carbon dioxide is lost. As the concentration of carbon dioxide declines, more gaseous ammonia will escape, and the pH will decrease.

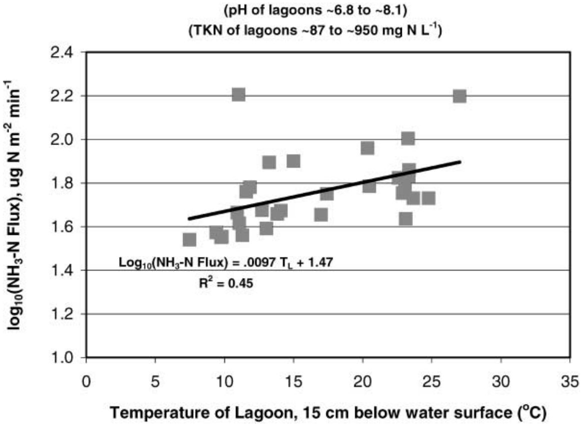

Fig. 4. Daily average ammonia-nitrogen flux vs. daily average lagoon surface water temperatures. Lagoon temperature was measured ~ 15 cm below the lagoon surface. Only days with at least 18 hr of measurements for both parameters appear on this graph.

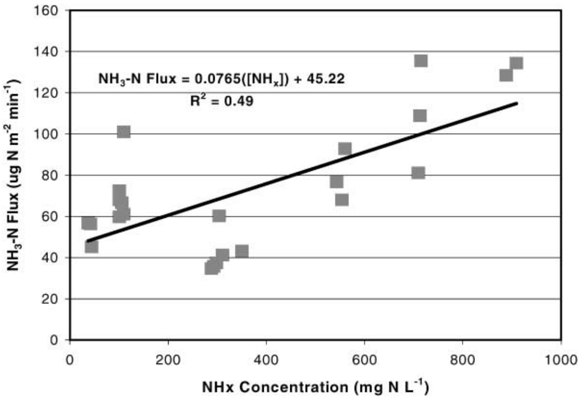

Fig. 5. Average daily ammonia-nitrogen flux vs. lagoon aqueous phase NH_x concentration. NH_x is the total ammonia nitrogen ($NH_3 - N + NH_4^+ - N$).

3.4. $[NH_x]$, *TKN*, *and ammonia flux*

Table 3 shows the average $[NH_x]$ and TKN values found in each lagoon, along with the corresponding range of values. Average $[NH_x]$ ranged from 37 to $909\,mg\,N\,l^{-1}$ and average TKN values varied from 87 to $950\,mg\,N\,l^{-1}$. In this experiment, we can compare $[NH_x]$ values from several different lagoons and plot them together to determine if it is an important parameter in controlling NH_3 flux from hog waste and treatment lagoons, as shown in Fig. 5. The average daily flux of NH_3-N is plotted against the daily measured $[NH_x]$ in the lagoon. A linear relationship with a significant correlation ($r^2 = 0.49$) was found between $[NH_x]$ and NH_3-N flux. Previous studies have found that the accumulated flux of ammonia is linearly related to the amount of total ammoniacal nitrogen ($NH_3 + NH_4^+$) in the slurry (Aneja et al., 2000b; Sommer et al., 1991). Judging from the coefficient of correlation ($r^2 = 0.49$), however, $[NH_x]$ is not the only factor affecting flux in the system.

$[NH_x]$ in each lagoon varied during the individual measurement periods, with the smallest range being

$7\,\mathrm{mg\,N\,l^{-1}}$, and the largest at $200\,\mathrm{mg\,N\,l^{-1}}$ (Table 3). Long-term fluctuations in $[\mathrm{NH}_x]$ will depend on the changes in animal number, animal weight, and their feeding pattern over the period of consideration. Operations which keep roughly the same number of animals and feeding habits throughout the year should provide a relatively uniform input of fresh waste into the lagoon during every season, keeping $[\mathrm{NH}_x]$ consistent all year. Although the level of the lagoon rises and falls due to varying rates of evaporation and precipitation during different seasons, these factors should cause relatively minor fluctuations in the nitrogen concentration of the lagoon (Chauhan, 1999).

Variation in the values of TKN should be fairly consistent with $[\mathrm{NH}_x]$, since the only difference between the two measurements is the amount of organic nitrogen in the system. Our analysis shows that TKN has nearly the same relationship to $\mathrm{NH_3}$-N flux as $[\mathrm{NH}_x]$.

In this study, both lagoon temperature ($r^2 = 0.45$) and $[\mathrm{NH}_x]$ ($r^2 = 0.49$) were found to be important factors controlling the emission rate (flux) of $\mathrm{NH_3}$ from lagoon surfaces. Using $[\mathrm{NH}_x]$ and lagoon temperature as major components, $\mathrm{NH_3}$-N flux may be predicted by a multiple regression equation ($r^2 = 0.74$)

$$\mathrm{Ln(NH_3\text{-}Nflux)} = 1.0788 + 0.0406T_\mathrm{L} + 0.0015([\mathrm{NH}_x]), \quad (8)$$

where $\mathrm{NH_3}$-N flux is expressed in $\mathrm{\mu g\,N\,m^{-2}\,min^{-1}}$, T_L is lagoon surface water temperature in °C, and $[\mathrm{NH}_x]$ is total ammonia-nitrogen concentration expressed in $\mathrm{mg\,l^{-1}}$.

The emissions in this study are generally lower than those determined by Aneja et al. (2000a). It appears that the difference is in part a function of the much stronger dependence of $\mathrm{NH_3}$-N on lagoon temperature observed by Aneja et al. (2000a) and lower pH in the present study. We can see the temperature difference in the slope terms of the observational models developed from the two studies:

$$\log_{10}(\mathrm{NH_3\text{-}N\,flux}) = 0.048T_\mathrm{L} + 2.1 \quad \text{Aneja et al. (2000a)},$$

$$\log_{10}(\mathrm{NH3\text{-}N\,flux}) = 0.0097T_\mathrm{L} + 1.47 \quad \text{(this study)}.$$

Also, the average value of TKN observed by Aneja et al. (2000a) ($650\,\mathrm{mg\,N\,l^{-1}}$) is higher than the average value across sites in this study ($570.0\,\mathrm{mg\,N\,l^{-1}}$). Higher TKN, aqueous $[\mathrm{NH}_x]$ concentrations, and pH found by Aneja et al. (2000a) may be the reason for the larger emission determined by that study. While it is likely that there are factors other that temperature and pH imposing differences in the emissions determined in the two studies, identification of these factors continues to be explored by the use of a coupled mass transfer and chemical reaction model (Aneja et al., 2000b).

4. Conclusions

This study shows that temperature, NH_x concentration, and pH in the lagoon are significant predictor variables for lagoon $\mathrm{NH_3}$-N flux. Across the lagoons in this study, $[\mathrm{NH}_x]$ in lagoon solution and lagoon surface water temperature explain about 75% of the variation in daily average $\mathrm{NH_3}$-N flux values. The pH values (pH range 6.8–8.1) of the lagoons are lower than the earlier study (pH range 7.5–8.5, Aneja et al., 2000a). The fluxes measured in this study (40.7–$120.3\,\mathrm{\mu g\,N\,m^{-2}\,min^{-1}}$) are lower than those found by Aneja et al. (2000a), who also used the same measurement technique. It appears that this difference is in part the result of a larger dependence of flux on temperature, higher NH_x concentrations, and higher pH observed by Aneja et al. (2000a). Comparison of these two studies suggests that while the factors controlling the flux, as determined using the dynamic flow-through chamber method, are similar across sites, the strength of these individual factors may differ. Continued research is needed to further examine the differences in observational models describing lagoon $\mathrm{NH_3}$-N flux.

Recommendations for future research in this area may be provided based on our experimental methodology. Ideally, measurements should be made over a wide range of lagoon sizes and types throughout the year, covering the range of yearly lagoon surface temperatures, pH, $[\mathrm{NH}_x]$, and other parameters and results compared with fundamental coupled mass transfer and chemical reaction model The dynamic flow-through chamber appears to provide a good estimate of ammonia flux.

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