

UNC-WRRI 2000-329

CHARACTERIZATION OF ATMOSPHERIC AMMONIA EMISSIONS FROM SWINE WASTE STORAGE AND TREATMENT LAGOONS

by

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The research on which this report is based was financed by the Department of Environment and Natural Resources, Division of Air Quality, through the N.C. Water Resources Research Institute.

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Project No. 50214
June 2000

Acknowledgments

This research was funded by the Division of Air Quality, North Carolina Department of Environment and Natural Resources (NC DENR) (Contract No. EA8001), and Water Resources Research Institute (WRRI) (Contract No. EA7003).

The cooperation extended by the North Carolina Pork Council is greatly appreciated. We sincerely acknowledge Mr. George Murray, Mr. R. Wooten, Mr. R. McCulloch, S. Few of the Division of Air Quality; Mr. T. Pierce of the U.S. Environmental Protection Agency; and Mr. Y. Li, Mr. B. Bunton, Mr. B. Malik, N. Agrawal and Ms. D. Nelson of our Air Quality Research Program at North Carolina State University for the technical discussions and review of the manuscript; and Ms. M. DeFeo and Ms. P. Aneja in the preparation of the manuscript.

Financial support does not constitute an endorsement by NC DENR and WRRI of the views expressed in the article/report, nor does mention of trade names of commercial or noncommercial products constitute endorsement or recommendations for use.

Abstract

Fluxes of atmospheric ammonia-nitrogen ($\text{NH}_3\text{-N}$, where $\text{NH}_3\text{-N} = (14/17)\text{NH}_3$) from an anaerobic ~ 2.5 hectares ($1 \text{ ha} = 10,000 \text{ m}^2$) commercial hog waste storage lagoon were measured during the summer of 1997 through the spring of 1998 in order to study the seasonal variability in emission of $\text{NH}_3\text{-N}$ and its relationship to lagoon physicochemical properties. Ammonia-nitrogen fluxes were measured during each season (summer, fall, winter, and spring) using a dynamic flow through chamber system. Measured lagoon physicochemical parameters included surface lagoon temperature (T_λ °C, ~ 15 cm below surface), lagoon pH, and Total Kjeldahl Nitrogen (TKN). The pH and TKN of the surface lagoon water ranged from 7 to 8 pH units, and 500 to 750 mg N L^{-1} , respectively. The largest fluxes were observed during the summer (August '97) (mean $\text{NH}_3\text{-N}$ flux = $4017 \pm 987 \mu\text{g N m}^{-2} \text{ min}^{-1}$). Fluxes decreased through the fall (December '97) months ($844 \pm 401 \mu\text{g N m}^{-2} \text{ min}^{-1}$) to a minimum flux during the winter (February '98) months ($305 \pm 154 \mu\text{g N m}^{-2} \text{ min}^{-1}$). Emission rates increased during spring (May '98) ($1706 \pm 552 \mu\text{g N m}^{-2} \text{ min}^{-1}$), but did not reach the magnitude of fluxes observed during the summer. Lagoon emissions in Eastern North Carolina were estimated to constitute $\sim 33\%$ of total $\text{NH}_3\text{-N}$ emissions from commercial hog operations in North Carolina based on current inventories for $\text{NH}_3\text{-N}$ emissions published by the North Carolina Division of Air Quality (NCDENR). The ammonia flux may be predicted by an observational model $\log_{10}(\text{NH}_3\text{-N Flux}) = 0.048 T_\lambda + 2.1$.

Keywords: ammonia flux, swine lagoon, dynamic chamber, flux model.

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Conclusions

The data presented in this paper adds to the growing knowledge of NH_3 flux from animal agricultural practice. The intensive measurements conducted during 1 August-15 August, 1997, presented us with typical summer temperatures observed in North Carolina and gave the highest flux estimates of the year. Using the dynamic chamber system, the average flux measured in the summer of 1997 was $4017 \pm 987 \mu\text{g N m}^{-2} \text{ min}^{-1}$. The averages during the spring, fall, and winter seasons were 1706 ± 552 , 844 ± 401 , and $305 \pm 154 \mu\text{g N m}^{-2} \text{ min}^{-1}$, respectively. We found that the NH_3 flux displays a diurnal variation which is highly correlated with lagoon surface water temperature and reaches a maximum between 3 and 6 PM. Ammonia flux is found to vary exponentially with lagoon surface water temperature. The pH and TKN levels in the lagoon remained relatively constant at an average value of ~ 7.5 pH, and $\sim 650 \text{ mg N L}^{-1}$, respectively.

The emission factors obtained by this research and other similar measurements on swine agriculture are summarized in Table 5. In general, there is reasonable agreement between researchers making NH_3 flux measurements from swine agriculture. The emissions factors listed represent emissions values from varying locations around the globe. The scatter in the emission factors may be explained by differences in meteorology, management practices, animal feeds, and experimental error. Using remotely sensed lagoon surface area data we have also estimated that lagoon ammonia emissions in eastern North Carolina comprise approximately 33% of total swine NH_3 emissions in North Carolina.

It is reasonable to assume that animal agriculture will be a continued source of significant atmospheric NH_3 emissions in Eastern North Carolina. Moreover, Walker *et al.* (1998) have demonstrated that increasing trends in ammonium concentration in precipitation in eastern North Carolina are directly correlated to the ever-expanding hog population in this region. Atmospheric deposition of NH_x will undoubtedly continue to impact nearby ecosystems with the potential of enhancing eutrophication and soil acidification. Furthermore, enhanced NH_3 emissions will enhance particulate matter formation in the region, which reduces visibility (Barthelmie and Pryor, 1998) and also causes health problems for workers in livestock agriculture (Reynolds and Wolf, 1988; Michaels, 1999). Another concern associated with NH_3 emission is its potentially harmful odor. To address these concerns and outline possible control strategies, further research is required in modeling the fate of NH_x with regional deposition models.

1. Introduction

1.1 Background

Atmospheric ammonia (NH_3) emissions have garnered increased interest in the past few years, due in part to the detrimental effects of excess nitrogen deposition to nutrient sensitive ecosystems (Aneja *et al.*, 1998a; Asman *et al.*, 1998; Nihlgard, 1985; Van Breemen *et al.*, 1982). Moreover, NH_3 is the primary gaseous base found in the atmosphere, and it is therefore fundamental in determining the overall acidity of precipitation (Warneck, 1988), cloudwater (Li and Aneja, 1992), and atmospheric aerosols (Lefer *et al.*, 1999). Ammonia emissions contribute substantially to atmospheric nitrogen loading and may contribute about the same order of magnitude as emissions of NO in some parts of the world (Asman *et al.*, 1998; Steingröver and Boxman, 1996). The impact of atmospheric NH_3 deposition may be substantial, as reduced nitrogen species are thought to be more biologically active than oxidized nitrogen species in coastal and estuarine ecosystems (Paerl, 1997). In the atmosphere, NH_3 can react with acidic species to form ammonium sulfate, ammonium nitrate or ammonium chloride, or it may be deposited to the earth's surface. The spatial scale of a particular NH_3 source's contribution to atmospheric nitrogen deposition will be governed in part by the gas-to-particle conversion rate of NH_3 to NH_4^+ . Because of the short lifetime of NH_3 in the atmosphere ($\tau = 1\text{-}5$ days or less) (Warneck, 1988), low source height, and relatively high dry deposition velocity (Asman and van Jaarsveld, 1992) it may deposit near its source. However, ammonium (NH_4^+) aerosols, with atmospheric lifetimes on the order of $\tau = 1\text{-}15$ days (Aneja *et al.*, 1998b) will deposit at larger distances downwind of sources.

There are several environmental consequences associated with atmospheric NH_3 and its deposition; including particulate matter formation, soil acidification, aquatic eutrophication, and, near strong sources, odor emanation. In Great Britain and the Netherlands, which have dense spatial distributions of animal operations, soil acidification is a major environmental problem (Aben and Dekkers, 1996; Van Breemen *et al.*, 1982). Van Breemen *et al.*, 1982 identified deposition of ammonium sulfate as the major cause of soil acidification in the Netherlands because the oxidation of NH_4^+ via nitrifying bacteria releases 2 H^+ ions into soil. Nihlgard (1985) implicates NH_4^+ in Europe's forest decline, as nitrogen "over-saturated" trees succumb to wind, drought and parasitic damage. Coastal Plain river systems in North Carolina (NC) have been under the influence of nutrient loading for several years (Aneja *et al.*, 1998c; Paerl, 1997, 1995). Estimates suggest that atmospheric deposition may contribute 35-60% of total nitrogen loading to North Carolina coastal waters (Paerl, 1995). The increase in nutrient loading over the past several years is related to agricultural management, human population growth, and increasing animal production. In July 1995, the appearance of the dinoflagellate *Pfiesteria* and its association with several large fish kills have resulted in efforts to reduce nitrogen loading into the Neuse River Basin (Burkholder and Glasgow, Jr., 1997). A successful reduction strategy requires an accurate nitrogen budget for affected ecosystems and reliable source apportionment of nitrogen inputs to such systems. From an atmospheric standpoint, accurate emission factors for NH_3 sources, as well as measurement-based estimates of wet atmospheric deposition and dry deposition to various surface types are essential. This study addresses NH_3 emissions from swine waste lagoons, as this source is believed to contribute a substantial fraction of total NH_3 emissions in North Carolina (Aneja *et al.*, 1998b).

1.2 Ammonia Emissions

Ammonia is an important contributor to the atmospheric nitrogen budget; however, its sources and their emission strengths have received scant attention in the United States. The major global sources of ammonia include the decay of domestic livestock waste, volatilization losses from fertilizers, emissions from soils and biomass burning. However, the largest contributor of ammonia to the global budget is domestic animal waste (Bouwman *et al.*, 1997; Dentener and Crutzen, 1994; Schlesinger and Hartley, 1992; Warneck, 1988; Buijsman *et al.*, 1987). A preliminary nitrogen emission inventory for North Carolina (Table 1), suggests that ammonia emissions are primarily associated with livestock farming. Table 1 also reveals that swine operations contribute ~20% towards North Carolina's nitrogen emissions inventory and comprise ~47% of total NH_3 emissions in the state.

North Carolina has witnessed intense growth in its hog industry over the last decade (Figure 1).

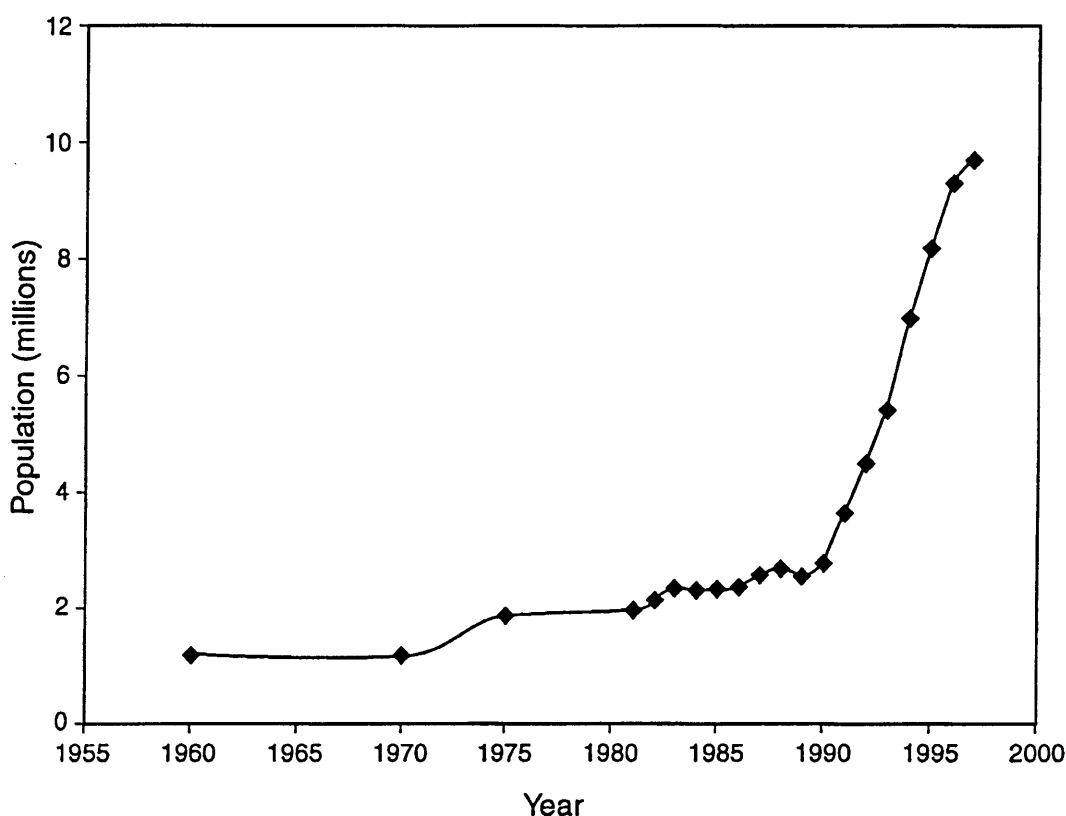


Figure 1. Trends in swine population in North Carolina, 1960-1997. (Source: NCDA, 1998).

More than 90% of the states hog population resides in the Coastal Plain region (Walker *et al.*, 1998; Walker, 1998) where there is greater potential to directly impact coastal estuaries (Figure 2). The six most highly populated counties in this region have an average hog population density of ~528 hogs km^{-2} (Table 2), whereas the average hog population density for the remainder of the Coastal Plain region is ~65 hogs km^{-2} (Walker *et al.*, 1998). Ammonia emissions from these six Coastal Plain counties account for approximately 36% of total statewide NH_3 emissions, with emissions from swine operations accounting for 77% of total NH_3 emissions within this six county region. Using source-receptor modeling, Walker *et*

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

Source ¹	Nitrogen Species Emitted ²	Estimated Tons of Nitrogen Emitted per Year ³	% of Total N ⁴
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	9,926	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	8,270	2.5
“Other” Chickens (1995)	NH ₃	6,476	2.0
NH ₃ Point Sources (1995)	NH ₃	1,665	0.5
Total		330,743	100.0

¹Nitrogen calculated From NO_x emissions assumes 100% NO₂ though the actual proportion is closer to 95%. Thus NO_x – N (tons) * (14/46) and NH₃ – N (tons) = NH₃ (tons) * 14/17).

²NO_x emission taken from DAQ inventories developed for modeling purposes; NH₃ emissions based upon factors presented in R. Battye, W. Battye, C. Overcash, and S. Fudge, 1994. Development and Selection of ammonia emission factors, Final report to U.S. Environmental Protection Agency (EPA), August 1994, and production statistics from the NSDA.

³Two minor ammonia sources, together totaling < 6,000 tons statewide, have been omitted. Factors for these, emissions from sewage treatment plants and emission associated with human breathing, are based upon vary limited data are currently being reevaluated.

⁴Relative proportions of NO_x = 58%, NH_x = 42%.

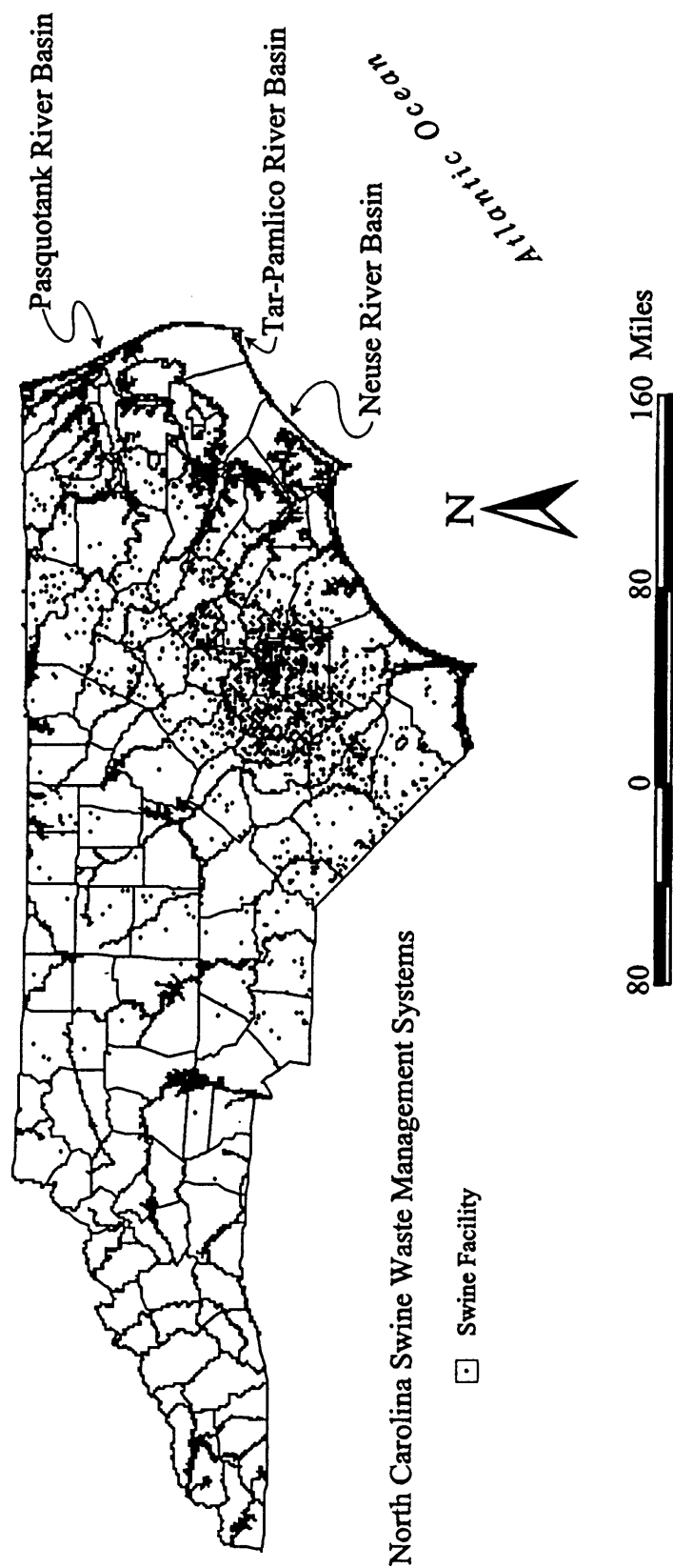


Figure 2. North Carolina swine waste management systems. Confined feedlots registered with NC DENR as required by 15A NCAC2H.0217 rule for waste not discharged to surface waters.

Table 2. Top six North Carolina county hog population densities.

County	Hogs km ⁻²
Duplin	1040
Sampson	752
Greene	560
Wayne	396
Bladen	309
Lenoir	304

Swine population statistics provided by the North Carolina Department of Agriculture (NCDA, 1998) for animal populations as of 1997.

al. (1998) have shown that under certain meteorological conditions NH₃ emissions from this six county area enhance wet deposition of NH₄⁺/NH₃ at National Atmospheric Deposition Program/National Trend Network (NADP/NTN) sites up to 80 km away. The precipitation samples were collected by wet-only collector (AeroChem Metrics Model 301 Wet/Dry Collector, NADP/NTN (1998)). This distance is sufficient to allow for deposition to nitrogen sensitive coastal and estuarine ecosystems. This illustrates the importance of quantifying NH₃ emissions from swine operations and properly relating these emission estimates to those factors which control emission rates. This information is necessary as inputs to atmospheric transport and deposition models such as the Regional Acid Deposition Model (RADM) currently being modified to accurately address the atmospheric transport and deposition of NH_x (=NH₃ + NH₄⁺). Such models will help policy makers assess the impact and magnitude of atmospheric nitrogen deposition on local and regional scales.

Emission factors used thus far for generating preliminary N.C. ammonia emission inventories for various animal husbandry operations are largely based on European work (Battye *et al.*, 1994). The European factors must be verified or refined for conditions in North Carolina. An initial step in this process is the development of swine factors since total emissions from swine are greater than other animal categories in North Carolina. There are four principal sources of NH₃ emissions on a current commercial hog operation: hog production houses, waste storage and treatment lagoon, land application of lagoon slurry to adjacent cropland, and subsequent reemission of NH₃ from the soil. Lagoon NH₃ emissions arise as urine and feces are flushed with water from the hog houses and discharged into the lagoon. Gas and liquid phase mass transfer processes are thought to be equally important in determining the overall desorption/absorption rate of ammonia (Leuning *et al.*, 1984). As the slurry (~98% water (Bicudo *et al.*, 1999)) is stored in the lagoon, urea is hydrolyzed by the enzyme urease, present in feces, to produce NH₃ and carbon dioxide (Aarnink *et al.*, 1995; Miller and Gardiner, 1998).

The primary objective of this study was to measure the atmospheric flux of NH_3 from a swine waste storage and treatment lagoon during the four predominant seasons at an intensively managed industrial hog operation in order to develop emission factors. The secondary objective was to parameterize the NH_3 flux process with respect to changes in lagoon physicochemical parameters (lagoon temperature, pH and total Kjeldahl nitrogen (TKN)) for use in air quality models.

2. Methods and Materials

2.1 Sampling Site

Flux measurements were made at a farrow to finish commercial hog operation in Sampson County, North Carolina. The farm consisted of 13 hog production houses housing approximately 10,000 animals: 1212 sows and boars (average weight ~181 kg each), 7,480 finishers (~61 kg each), and ~1410 suckling pigs (~11 kg each) (R.B. McCulloch, Division of Air Quality, NCDENR, Raleigh, NC, Personal Communication, 1998a). The waste from the hog sheds (urine and feces) was flushed out with recycled lagoon water and discharged into the lagoon from the top ("top-loading"). The lagoon itself was an above ground anaerobic system with sloping sides that reached a maximum depth of ~4m at the center. The surface area of the lagoon was ~25,000 m² (~100 m x ~250 m).

2.2 Slurry composition and analysis

To determine the concentration of total nitrogen (aqueous ammonia, ammonium, and nitrates) in the slurry, lagoon water samples were taken once every day during the flux sampling periods and submitted to the Department of Soil Science, North Carolina State University for analysis. Samples were analyzed for total Kjeldahl Nitrogen (TKN) using a digestion procedure, which converts all N in the lagoon sample to NH₄⁺. The NH₄⁺ concentration in the sample was determined by colorimetry.

2.3 Flux measurements

Ammonia flux was measured using a dynamic chamber system (Aneja *et al.*, 1996). Summer measurements were made from 1 August, 1997 to 15 August, 1997. The fall (December, 1997) and winter (February, 1998) measurements lasted intermittently for 6 and 10 days, respectively. Flux measurements were discontinued during precipitation events. In spring, ammonia flux measurements were made from 16 May, 1998, to 27 May, 1998. In general, lagoon water temperature was monitored continuously with a temperature probe (Fascinating Electronics, Deer Island, Oregon) immersed ~15 cm below the lagoon water surface ~48 cm from the chamber; and the lagoon pH was monitored continuously using a double junction submersible electrode (Cole Parmer, Vernon Hills, Illinois), also placed ~48 cm from the chamber and adjacent to the temperature probe. However, some measurements of temperature and pH were recorded manually.

2.4 Chamber design and operation

The dynamic chamber used in this study is an FEP Teflon-lined (5 mil thick) open bottom cylinder (diameter ~27 cm, height ~42 cm, and volume ~25 liter) inserted into a 1.22 m x 1.22 m floatable platform. When the platform and chamber were placed on the lagoon, the chamber penetrated the lagoon surface to a depth of ~4 cm forming a seal between the lagoon surface and the air within the chamber. The placement of the chamber on the lagoon surface was performed in a statistically random manner. Figure 3 shows a schematic of the floating dynamic chamber system. Compressed zero-grade air (National Welders, Raleigh, NC) was pumped through the chamber at a constant flow rate of ~4.73 λ min⁻¹, 4.14 λ min⁻¹, 2.69 λ min⁻¹, and 2.36 λ min⁻¹ for the summer, fall, winter, and spring field measurement periods, respectively. The air in the chamber was well mixed continuously by a motor driven Teflon impeller (~20 cm diameter at ~50 rpm). The length of the Teflon tubing (0.64 cm o.d.) connecting the chamber and the ammonia analyzer was less than 10 m.

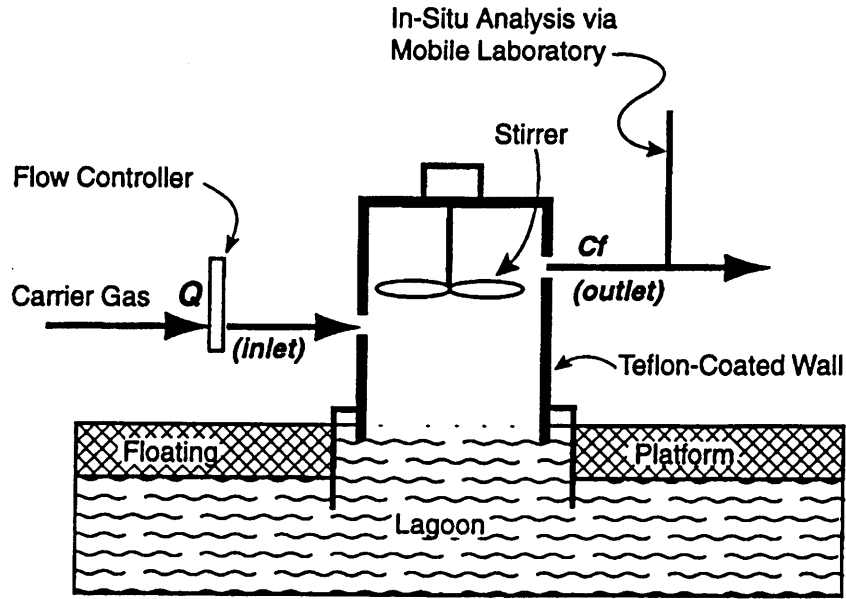


Figure 3. Schematic of a dynamic flow-through chamber. The chamber fits on a floating platform which is placed on the surface of the waste treatment lagoon ~24 hours prior to start to measurement to minimize disturbances.

2.5 Flux calculation

The mass balance for NH_3 in the chamber is given by

$$\frac{dC}{dt} = \left[\frac{Q [C]_0}{V} + \frac{JA_L}{V} \right] - \left[\frac{LA_c [C]}{V} + \frac{Q [C]}{V} \right] - R \quad (1)$$

where A_L is the lagoon surface area covered by the chamber, A_c is the inner surface area of the chamber, V is the volume of the chamber, Q is the flow rate of carrier gas through the chamber, J is the emission flux, $[C]$ is the NH_3 concentration in the chamber, $[C]_f$ is the NH_3 concentration at the outlet of the chamber, L is the loss term by the chamber wall per unit area assumed first order in $[C]$ and R is the chemical production rate in the chamber.

Because compressed zero air was used as the carrier gas, there is no inlet concentration of ammonia, $[C]_0 = 0$, and for a well mixed chamber $[C]_f$ may be assumed to be equal to the NH_3 concentration everywhere in the chamber, $[C]$. Finally, at steady state the above equation reduces to

$$J = [C]_f \left[\frac{LA_c}{V} + \frac{Q}{V} \right] h \quad (2)$$

where h is the height of the chamber measured from the lagoon surface. The value of the total loss term, (L), was obtained (0.079 m min^{-1} and 0.059 m min^{-1} during summer and winter seasons, respectively) by conducting the surface loss experiment as proposed by Kaplan *et al.* (1988) and Aneja *et al.* (1996).

Once the chamber reached steady state conditions (~30 min of operation), the outgoing air was conducted through Teflon tubes to a Measurement Technologies 1000N stainless steel NH_3 converter which transformed the $N_T (= \text{NH}_3 + \text{R-NH}_2 + \text{NO} + \text{NO}_2)$ constituents of the sampled air into nitric oxide (NO) at $\sim 825^\circ\text{C}$ (Aneja *et al.*, 1978). The sample flow from the NH_3 converter was routed to an Advanced Pollution Instruments (API) Model 200 chemiluminescence based NO monitor where the transformed N_T concentration in parts per billion by volume (ppbv) was determined. Part of the flow from the chamber was bypassed directly to the API, which transformed to NO only the $\text{NO} + \text{NO}_2 (= \text{NO}_x)$ portion of N_T via a molybdenum converter heated to $\sim 350^\circ\text{C}$ (Aneja *et al.*, 1996; Fehsenfeld *et al.*, 1987). The API then determined the NH_3 concentration in surface lagoon air by subtracting the NO_x signal from the N_T signal ($\text{NH}_3 = N_T - \text{NO}_x$). The API was calibrated following written protocols using a Thermo Environment Instruments Inc. Model 146 gas dilution/titration instrument with a calibration gas mixture of NO in N_2 i.e., parts per million by volume (734ppmv) and compressed zero-grade air. A multipoint calibration on the API analyzer was performed before each set of intensive measurements and the instrument was zeroed and spanned daily during each measurement intensive. The early morning data gaps (Figure 4) represent the time period during which the daily zero/span procedure was performed on the ammonia analyzer. The efficiency of the ammonia converter was checked regularly using a known ammonia concentration. Laboratory tests using a known concentration of NH_3 have shown no measurable conversion of NH_3 to NO at 350°C within a molybdenum converter. Instrumentation was housed in a temperature controlled mobile laboratory (modified Ford Aerostar van).

3. Results and Discussion

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 Godfrey, 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 what wind velocities are at a height of 0.1 m (the height of the impeller above water-air interface) when 10 m wind heights are known. The power-law profile is given by:

$$\frac{V}{V_r} = \left(\frac{Z}{Z_r} \right)^m \quad (3)$$

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).

Throughout the measurement period during this study, mean wind velocities were between 1 and 4 m/s at a height of 10 m. Through the power-law profile above this equates to wind speeds between 0.6 and 2.4 m/s at a height of 10 cm similar to wind speeds inside the chamber (measured with a hot wire anemometer between ~1 and 2.5 m/s) 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.

3.1 Seasonal fluxes

Table 3 summarizes the average fluxes for each season. Using seasonal averages, the percent of total yearly flux attributable to summer months is ~60%. The change in the daily flux pattern for each season can be seen in Figure 4 together with one standard deviation (± 1 s.d.). Each data point in this figure represents an average of the flux measured at a particular time over the entire measurement period. In general, $n=12$ (where n is the number of flux values that made up the average) for the summer and spring seasons, $n=4$ for the winter season except between 11AM-5PM where $n=8$, and $n=6$ for the fall season. The morning data gaps (Figure 4) represent the time period during which the daily zero/span procedure was performed on the ammonia analyzer. The analyzer was also multipoint calibrated regularly during the same time period. The reasons for the slight flux increase during morning hours, prior to the daily zero/span procedure is not known. However, ammonia desorption from the inner surfaces caused by morning temperature increase may be a possibility (Williams et al., 1992, Adema et al., 1990).

Table 3. Summary table of average daily $\text{NH}_3\text{-N}^{(a)}$ fluxes by season.

	Mean ^(b)	Maximum	Minimum
Summer '97	4017 (987) ^(c)	8526	2358
Fall '97 ^(d)	844 (401)	1913	369
Winter '98 ^(e)	305 (154)	695	90
Spring '98	1706 (552)	3594	851

^(a) $\text{NH}_3\text{-N}$ flux = (14/17) NH_3 flux.

^(b)Units of daily flux are $\mu\text{g N m}^{-2} \text{ min}^{-1}$.

^(c)Numbers in parentheses are one standard deviation.

^(d)All values measured from 11AM to 5PM EST.

^(e)Measurements were made on Feb 1, 2, 8, 15, 18, 20, 21, 22, 23, 25, and 26 1998 (11 AM-5 PM EST) with 21, 22, and 25 Feb being diurnal variations.

3.2 Lagoon temperature and ammonia flux

The pronounced summer maximum flux suggests that temperature is an important factor regulating the loss of NH_3 from the waste lagoon to the atmosphere. In this study the relationship between lagoon temperature and NH_3 flux is examined over a relatively wide range of temperatures ($\sim 4^\circ\text{C}$ to $\sim 40^\circ\text{C}$). Table 4 lists average lagoon surface temperatures measured during each season. We observed an exponential ($r^2 = 0.78$) relationship between NH_3 flux and lagoon water temperature measured over the year as illustrated in Figure 5. Each point in this figure represents an hourly averaged NH_3 flux ($n=6$, where n is the number of flux values in an hourly average) plotted against the corresponding hourly temperature measurement. A reason for the exponential relationship is that the liquid phase mass transfer coefficients of NH_3 in water are exponential functions of temperature in the range 5°C to 30°C , (Ibusuki and Aneja, 1984), and the dependence of Henry's Law on temperature (Dasgupta and Dong, 1986; Bates and Pinching, 1950). Thus, the transfer of NH_3 across the liquid-gas interface follows an exponential model; and the flux increases exponentially with surface lagoon temperature. The ammonia flux from the waste storage and treatment lagoon in North Carolina may be predicted by the observational model

$$\text{Log}_{10} (\text{NH}_3 - \text{N Flux}) = 0.048 T_\lambda + 2.1$$

where,

$\text{NH}_3 - \text{N Flux}$, $\mu\text{g N m}^{-2} \text{ min}^{-1}$

T_λ lagoon surface temperature, $^\circ\text{C}$.

The reason for the high NH_3 flux during summer is a combination of chemical and physical processes occurring within the lagoon. First, the decomposing waste sludge at the bottom of the lagoon acts as a

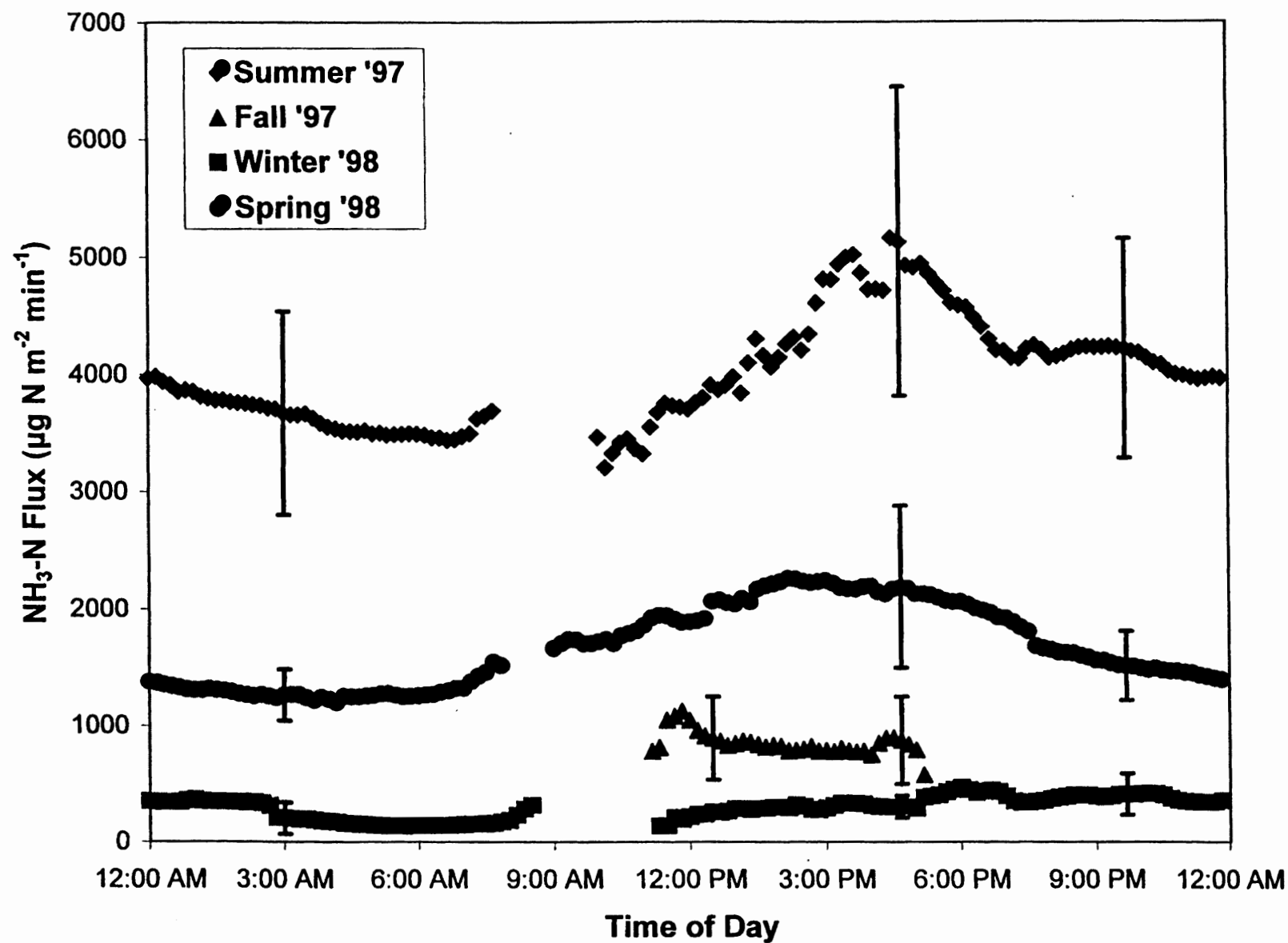


Figure 4. Daily trends of ammonia-N flux from the lagoon during the four predominant seasons. N=12 in summer, n=12 in spring, n=6 in fall, and n=4 in winter except 11 am and 5 pm where n=8. Vertical lines represent one standard deviation.

Table 4. Sampling periods for NH₃-N flux measurements and the mean, standard deviation, and range of lagoon surface (i.e., 15 cm depth) parameters measured during the N-NH₃ flux experiments.

Season	Sample Dates	Lagoon Temperature ^(a)	Lagoon pH	TKN ^(b)
Summer	1 Aug-15 Aug '97	30 (3.3) ^(c)	7.5 (.18)	648.1 (27.7)
		25.3-39.1	7.1-7.8	587-695
Fall	1 Dec-17 Dec '97 ^(d)	11.6 (2.2) ^(e)	8.0 (0.06)	663.3 (33.7)
		8.4-15.3	7.9-8.1	599-715
Winter	1 Feb-26 Feb '98 ^(f)	12.1 (2.1) ^(e)	7.8 (0.13)	641.7 (39.0)
		8.8-15.1	7.66-8.02	580-727
Spring	16 May-27 May '98	24.7 (3.2)	7.7 (0.06)	603.3 (48.2)
		20.4-35.9	7.64-7.81	540-720

^(a)Units of lagoon temperature are degrees Celsius.

^(b)Units of TKN nitrogen are mg N/L.

^(c)Numbers in parentheses are one standard deviation.

^(d)Flux measurements were made on December 1, 3, 5, 7, 15, and 17, 1997 (from 11 AM to 5 PM EST).

^(e)All values of lagoon temperature and pH measured from 11 AM to 5 PM EST manually.

^(f)Measurements were made on February 1, 2, 8, 15, 18, 20, 21, 22 23, 25, and 26, 1998 (from 11 AM to 5 PM EST), with 21, 22, and 25 February representing diurnal variations.

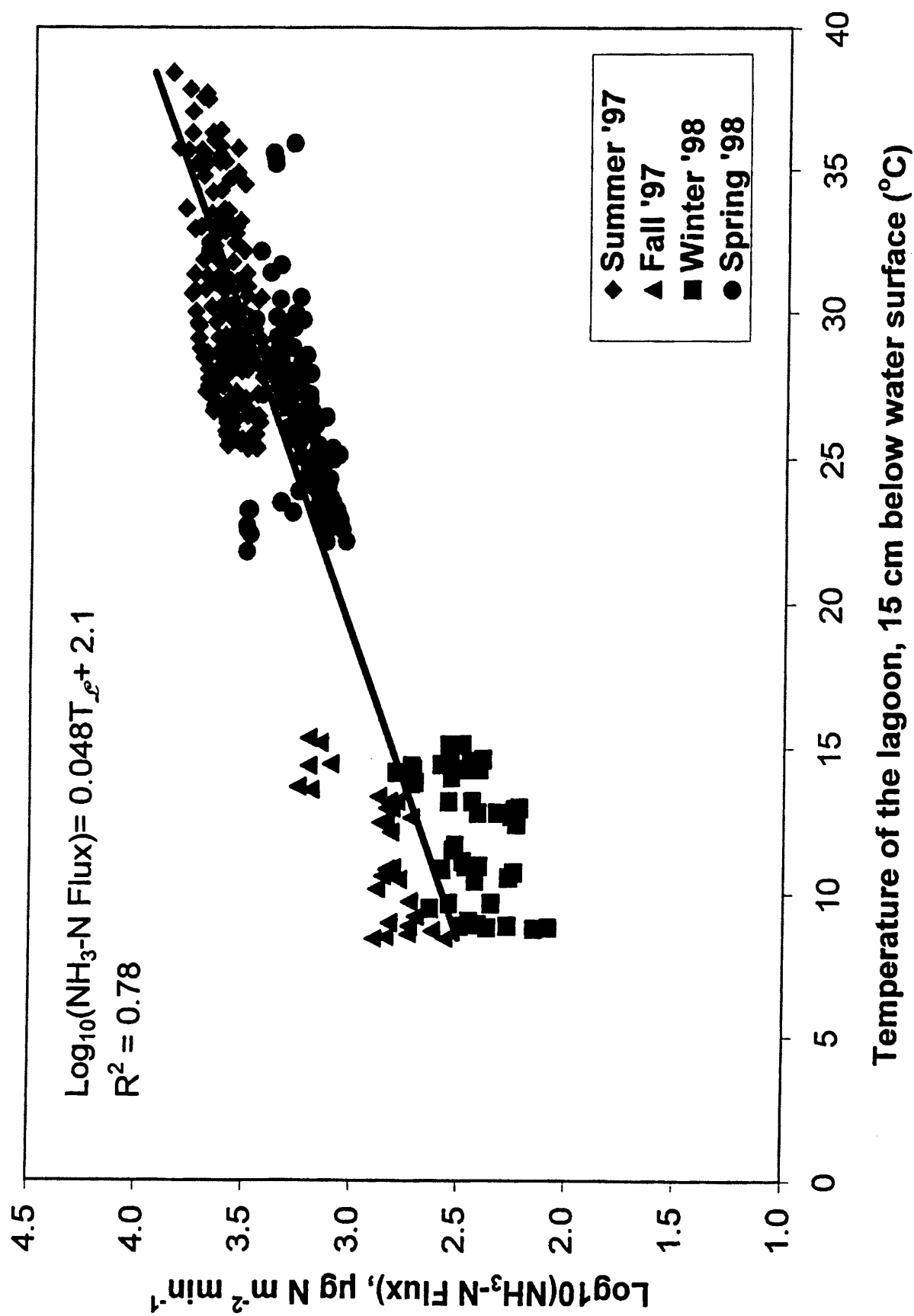


Figure 5. Log of hourly averaged ammonia-nitrogen flux from the lagoon surface plotted against lagoon aqueous phase surface temperature.

source of NH_3 , and the rate of decomposition increases with temperature. As NH_3 from the surface of the lagoon is volatilized, NH_3 formed from the decomposition of sludge at the bottom of lagoon diffuses upward and replenishes the volatilized NH_3 in the upper layers of the lagoon. Since this lagoon is not physically mixed by forced means, ammonia's principle mode of transport is through diffusion and mass transfer processes (Muck and Steenhuis, 1982). As illustrated by Ibusuki and Aneja (1984), higher temperatures increase the transfer rate of NH_3 across the liquid-gas interface. Thus, summer temperatures coupled with a readily available source of NH_3 results in summer fluxes ($4017 \pm 987 \mu\text{g N m}^{-2} \text{ min}^{-1}$) which are about an order of magnitude greater than those observed during the winter ($305 \pm 154 \mu\text{g N m}^{-2} \text{ min}^{-1}$) season.

Temperature (lagoon surface water and/or ambient) is a controller of NH_3 emissions in the boundary layer, and therefore NH_3 mixing ratios in the lower troposphere. Langford et al. (1992) have suggested that the "typical" seasonal and diel cycles of boundary layer NH_3 levels are, in general, a function of air temperature, with higher NH_3 mixing ratios associated with warmer temperatures. These seasonal NH_3 concentrations should therefore be manifest in ammonium ion concentration $[\text{NH}_4^+]$ in precipitation.

Multiple regression analysis of monthly volume-weighted ammonium concentration in precipitation at the National Atmospheric Deposition Program (NADP) site located in close proximity to the flux study, NC35 (located in Sampson County, latitude $35^\circ 01' 33'' \text{ N}$ and longitude $78^\circ 16' 21'' \text{ W}$ (NADP/NTN, 1998)), during the period 1982-1996 reveals a statistically significant ($p < 0.01$, $r^2 = 0.29$) positive correlation between mean monthly surface temperature and log of ammonium concentration (Figure 6).

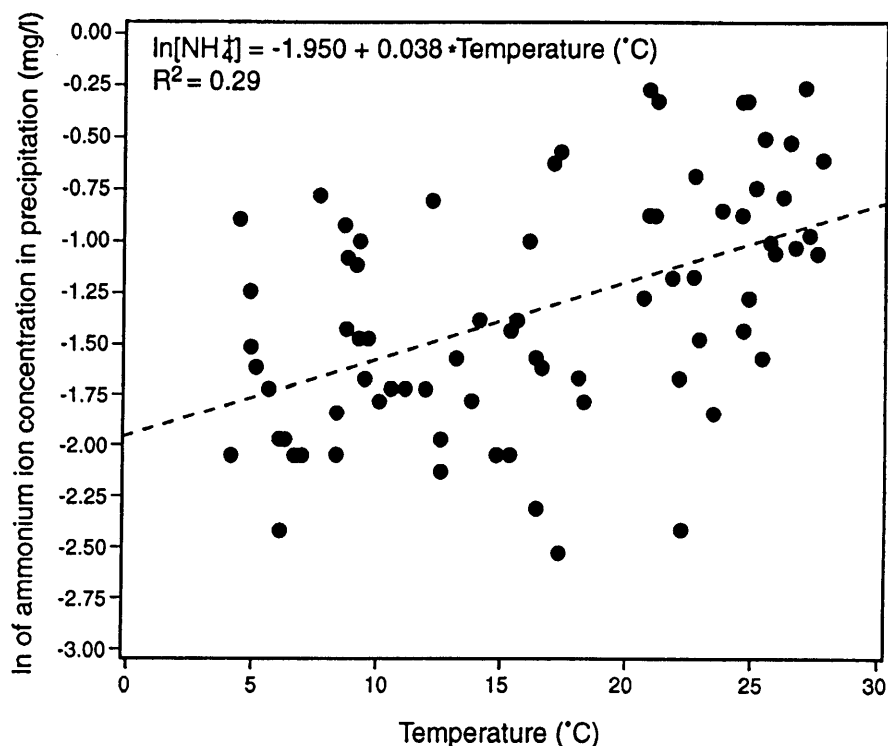
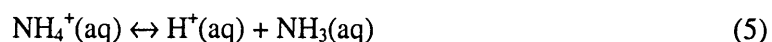
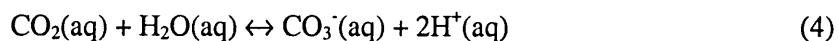


Figure 6. Natural log of monthly volume-weighted ammonia (NH_4) ion concentration in precipitation versus mean monthly atmospheric ambient temperature ($^\circ\text{C}$) for the NADP/NTN site NC35, located in Sampson County, during the period 1983-1996 (•) and the corresponding regression line (---).

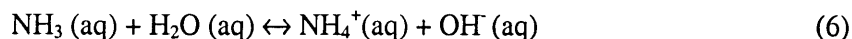
The present study has shown that volatilization of NH_3 from swine waste lagoons has a positively correlated exponential relationship with lagoon surface water temperature. At sites such as NC35, which are likely influenced by multiple nearby swine facilities, this may also contribute to the temperature dependence of ambient NH_3 concentrations and subsequent NH_4^+ concentrations in precipitation. Walker (1998) has shown a statistically significant seasonal cycle for $[\text{NH}_4^+]$ in precipitation, which maximizes during summer months, at NADP sites across North Carolina.

3.3 Lagoon pH and ammonia flux

The highest pH values were observed in the fall and winter seasons and ranged from 7.7 to 8.1 (Table 4). Koelliker and Minor (1973) have also observed pH values up to 8 in the fall and winter at a Missouri hog lagoon. The relative stability of lagoon pH throughout the year is due to the high buffer capacity of the slurry (Olesen and Sommer, 1993). The pH of the lagoon is maintained by the bicarbonate ion, formed as a product of the hydrolysis of urea and microbial conversion of organic matter (equation 4), which neutralizes the H^+ ion released into solution by $\text{NH}_4^+(\text{aq})$ as $\text{NH}_3(\text{aq})$ volatilizes (equation 5) (Sommer *et al.*, 1991; Fordham & Schwerdman, 1977):



Several published modeling studies (Dewes, 1996; Muck and Steenhuis, 1982; Vlek and Stumpe, 1978; Sommer *et al.*, 1991) report a positive relationship between lagoon NH_3 flux and pH. In lagoon slurry, NH_3 will be in solution with NH_4^+ according to the following equilibrium (Warneck, 1988):



The direction of the equilibrium in equation 6 depends on the pH. As the pH increases ($[\text{OH}^-]$ increases), the equilibrium shifts toward the left increasing the concentration of $\text{NH}_3(\text{aq})$ and hence the potential for volatilization. Thus, the proportion of the total NH_3 concentration that is ionized at any time is a function of lagoon pH. Equation 7 provides the theoretical relationship between the aqueous ammonia fraction, $F = \text{NH}_3/(\text{NH}_3 + \text{NH}_4^+)$, and pH of the lagoon (Loehr, 1984):

$$F = \frac{1}{1 + 10^{(\text{pK}_a - \text{pH})}} \quad (7)$$

where pK_a is the negative logarithm of the ionization constant for reaction (6). The relationship between flux and the pH over the range observed in this study (7.1 to 8.1) follows the theoretical prediction given by equation (7).

3.4 TKN and ammonia flux

A plot of the average daily flux over the entire year against TKN nitrogen for lagoon samples collected on the same day as the flux measurement is shown in Figure 7. We observed that the TKN levels remain relatively constant, varying between ~500 and ~750 mg N L^{-1} (Table 4). This stability is because the lagoon on which our measurements were taken is part of a steady state commercial operation at which animal weight and feed distributions are about the same throughout the year. Thus, the fresh waste input into the lagoon has a relatively constant nitrogen content which keeps lagoon TKN levels steady throughout the year. Across different seasons, the lagoon experiences various rates of evaporation and

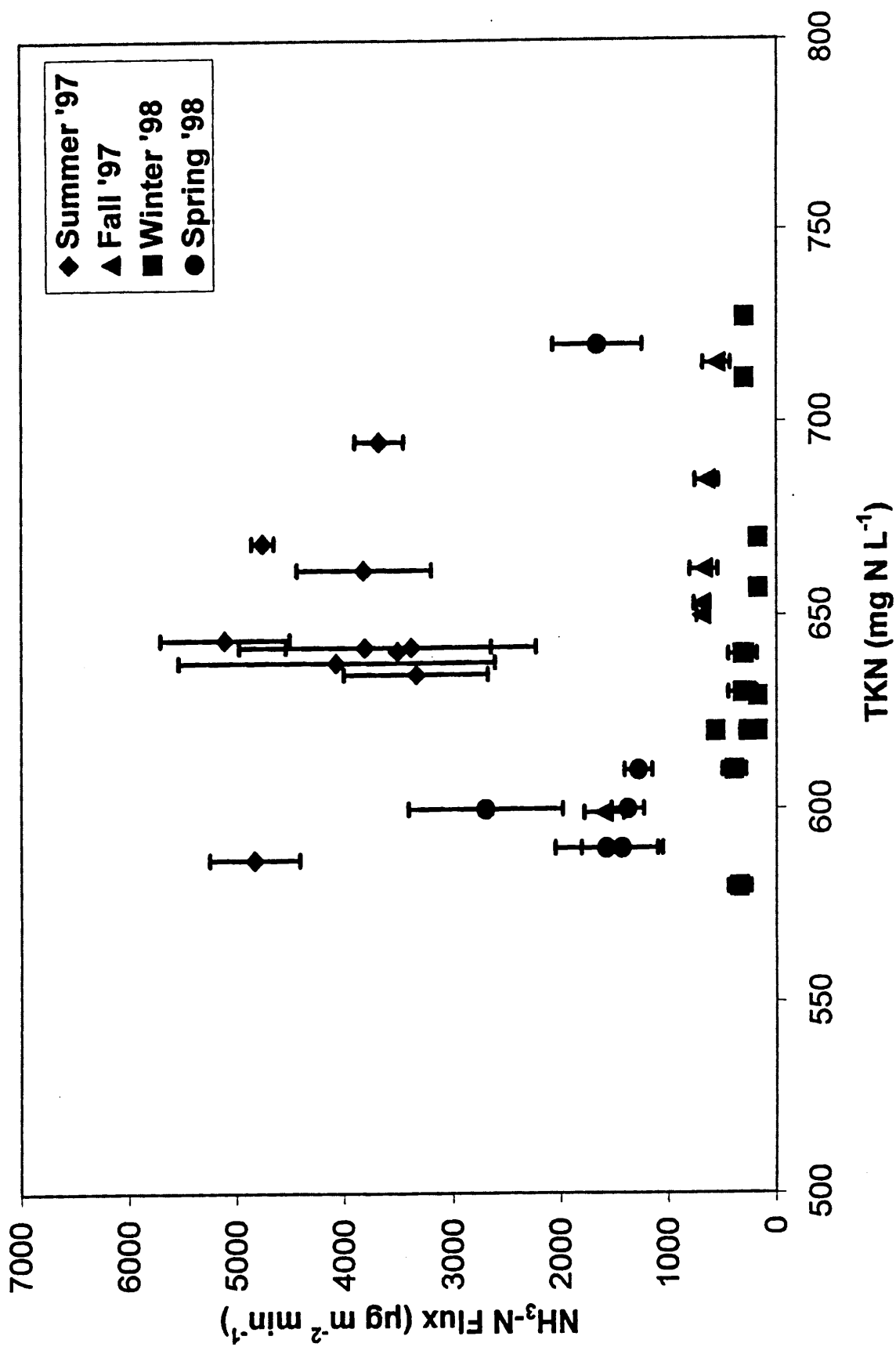


Figure 7. Average daily ammonia-N flux from the lagoon surface versus Total Kjeldahl Nitrogen (TKN) sampled from lagoon collected on the same day as the flux measurements. TKN measurement includes ammonia, ammonium, and nitrates in the aqueous phase.

Table 5. Ammonia-nitrogen emissions estimates and comparison of results.

Author	Emission Factors (kgN/animal/y)
Asman et al., 1992 [*]	4.41
Battye et al., 1994 [*]	7.58
van der Hoek, 1998	0.7-1.79
ECETOC (1994) ^{**}	1.0
Dragosits et al., 1998 [*]	3.18
McCulloch et al., 1998 [†]	4.88-9.52
This Study, 1998 ^{**}	
Summer	5.2
Spring	2.2
Winter	0.4
Fall	1.1
Average	2.2

^{*} Includes emissions from waste lagoons, animal houses, and surrounding crops.

^{**} Includes emissions from waste lagoons only.

[†] Derived from summer measurements only.

receives varying amounts of precipitation; however, these factors are likely to cause relatively minor fluctuations in the nitrogen concentration of the lagoon.

3.5 Scaling Ammonia Emissions Utilizing Remotely Sensed Data

Using the GIS spot satellite image of North Carolina for the period 1995-96, a statistically random sample of 50 lagoons was obtained for lagoon surface area in Eastern North Carolina (<http://www.lib.ncsu.edu/stacks/gis>). The 50 lagoons sampled for surface area, measured with the help of ARCVIEW 3.0, was 54 ha (i.e., ~1 ha/lagoon). The number of lagoons in Eastern North Carolina is ~2500 lagoons (NCDA, 1998). The seasonal average lagoon ammonia emission from this study is $\sim 1718 \pm 523 \mu\text{g N/m}^2/\text{min}$; and the total ammonia emissions from swine operations is ~68,540 tons N/yr (Aneja et al., 1998 b,c, and Table 1). From the emissions obtained in this study, it is therefore estimated that lagoon ammonia emissions in Eastern North Carolina comprise approximately 33% of total swine NH_3 emissions in North Carolina.

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