

ABSTRACT

ARKINSON, HEATHER LEIGH. Measurements, Modeling, and Analysis of Ammonia Flux from Hog Waste Treatment Technologies. (Under the direction of Viney Pal Aneja.)

Gaseous ammonia has a relatively short residence time in the atmosphere, depositing quickly back to the earth's surface. Excessive ammonia deposition can enhance environmental processes such as eutrophication of aquatic ecosystems. Atmospheric ammonia that does not deposit quickly combines with acidic species, such as sulfuric acid, nitric acid, and hydrochloric acid, to form ammonium aerosols. Ammonium aerosol has a longer residence time in the atmosphere and therefore travels farther distances from the source than gaseous ammonia does. Eventually, ammonium aerosol undergoes deposition, also affecting the earth's ecosystems. Domestic animal waste comprises the largest global source of atmospheric ammonia.

Ammonia emissions from agricultural operations have recently attracted attention in the state of North Carolina due to the rapid expansion of the state's swine industry over the past decade. In order to assess the potential effects of enhanced ammonia emission due to the large hog population, quantitative measurements of ammonia emissions from commercial swine operations must be made. Traditionally, hog operations utilize waste treatment lagoon and spray field technology for waste management. This study includes ammonia flux measurements from three farms with potential environmentally superior waste treatment technologies. These experimental technologies potentially produce lower ammonia emissions than the traditional waste management technology does. Field measurements are conducted over liquid waste surfaces, cropland soil surfaces, the surface of a covered waste treatment lagoon, and from a hog housing unit that contains a

belt removal system for waste. The measured ammonia emissions from the liquid waste surfaces have been parameterized by a multivariate physical and chemical model.

A coupled mass transfer with chemical reactions model predicts ammonia flux across a gas-liquid interface, such as an air-waste lagoon interface. Ammonia flux measurements made from the liquid waste components of experimental waste management systems and from traditional hog waste treatment lagoons validate the mechanistic model. A comparison between modeled and measured ammonia emissions demonstrates the strengths and weaknesses of both the mechanistic model and the field measurement system. Analysis of the measured and modeled ammonia fluxes with respect to environmental parameters reveals discrepancies between the two methods of quantification. This study strives to quantify ammonia flux from experimental and traditional hog waste treatment technologies via a combination of modeling and measurements in order to develop agricultural ammonia emission factors and to assess the extent of enhanced atmospheric ammonia loading due to hog operations in North Carolina.

Measurements, Modeling, and Analysis of Ammonia Flux from Hog Waste Treatment Technologies

By

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BIOGRAPHY

Heather Leigh Arkinson was born on April 5, 1978, in St. Albans, Vermont to James and Charlotte Arkinson. Much of Heather's interest in the environment, science and mathematics began at an early age. As a senior in high school at Bellows Free Academy, Heather participated in the Experimental Program to Stimulate Competitive Research at the University of Vermont, where she performed and presented her first scientific study, which involved the feeding patterns of birds in northern Vermont.

Upon graduating from high school in 1996, Heather entered McGill University in Montreal Canada to pursue a joint major in Atmospheric Sciences and Environmental Sciences. While at McGill she completed an Honors Atmospheric Chemistry Project involving the quantification of urban volatile alkenes via gas chromatography with preconcentration. She also performed an Environmental Science Seminar Research Project that investigated the carbon balance of the forests in the Mauricie Region in Quebec. Heather graduated with Distinction in 2000 with a joint major in Atmospheric and Environmental Sciences.

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CHAPTER I. INTRODUCTION

The Nitrogen Cycle

Nitrogen provides fundamental nourishment to all living matter. This essential nutrient allows organisms to emerge, grow, mature, and eventually die and decompose. Nitrogen travels throughout earth's natural spheres via complex transport mechanisms (Figure 1.1). The atmosphere contains a large portion of the nitrogen in existence, with approximately three fourths of the atmosphere's volume composed of dinitrogen (N_2). Nitrogen becomes available to the biosphere when dinitrogen from the atmosphere undergoes fixation, a process in which bacteria convert dinitrogen to nitrogen compounds that plants and animals can utilize. In aerobic environments of the biosphere, oxidized forms of nitrogen arise via nitrification, in which chemoautotrophic nitrifying bacteria convert reduced forms of nitrogen, such as ammonia (NH_3), to oxidized forms, such as nitrate (NO_3^-). The largely anaerobic process of denitrification returns oxidized nitrogen compounds to a reduced state, regenerating dinitrogen for the atmosphere. Oxidized and reduced nitrogen compounds from various stages of the nitrification/denitrification cycle can volatilize and enter the atmosphere or can seep into ground or surface water and enter the hydrosphere. Atmospheric nitrogen compounds, other than dinitrogen, undergo wet or dry deposition and return to the earth's soil and water surfaces (Warneck, 2000).

Ammonia

Ammonia, the most biologically active reduced form of nitrogen, plays a central role in the nitrogen cycle in the atmosphere, biosphere, lithosphere, and hydrosphere. In the soil, dead organic nitrogen undergoes mineralization, creating ammonium (NH_4^+) and ammonia, which exist in aqueous equilibrium. Ammonia also originates from urea, a

large component of animal excreta. The urease enzyme, produced by microbial organisms present in solid waste, breaks urea down into ammonia and carbon dioxide (Aarnink et al., 1995). Depending on ambient conditions such as pH and temperature, gaseous ammonia can volatilize from soil and liquid surfaces and enter the atmosphere (Warneck, 2000). As the dominant gas base specie in the atmosphere, ammonia readily combines with and neutralizes acidic compounds, including sulfuric acid (H_2SO_4), nitric acid (HNO_3) and hydrochloric acid (HCL), creating ammonium aerosols (Hewitt and Davison, 1998; Meszaros, 1993; Finlayson-Pitts, 1986). Ultimately, gaseous ammonia and ammonium aerosol undergo wet or dry deposition to the earth's surface (Warneck, 2000). The atmospheric lifetimes of gaseous ammonia and ammonium aerosol dictate the spatial scale of their sphere of influence.

Over the past few centuries, anthropogenic activities have perturbed the natural balance of ammonia and other nitrogen compounds. Currently, the human demand for food production requires the extensive use of nitrogen containing fertilizers, as well as the production of domestic livestock on a grand scale. Since ammonia volatilizes from the fertilizers and domestic animal waste associated with food production, agricultural operations give rise to an increased atmospheric load of gaseous ammonia and ammonium aerosol (McCulloch et al., 1998), which in turn enhances the deposition of nitrogen to soil surfaces and aquatic ecosystems (Walker et al., 2000; Paerl, 1995). Estimates of the global ammonia budget indicate that domestic animal waste emits approximately 20 to 35 Tg of ammonia to the atmosphere per year, representing approximately half of the annual global ammonia emissions (Table 1.1). Other natural and anthropogenic ammonia sources, such as soils and biomass burning, contribute

smaller portions to the global ammonia budget (Warneck, 2000; Dentener and Crutzen, 1994; Schlesinger and Hartley, 1992).

The number of commercial swine facilities in North Carolina has dramatically increased, with the state's hog population increasing from approximately 2.8 million in 1990 to 9.8 million in 2001 (Figure 1.2). Much of the expansion of North Carolina's hog industry has occurred in the Coastal Plain Region, with 63% of the state's hog population concentrated in a six county area encompassing Duplin, Sampson, Greene, Wayne, Bladen, and Lenoir counties (Figure 1.3). Current estimates indicate that atmospheric ammonia emitted from North Carolina's swine facilities accounts for 20% of the state's atmospheric nitrogen budget (Figure 1.4) and 47% of the state's atmospheric ammonia budget (Figure 1.5). Ammonia volatilizes from four principal sources at swine facilities, namely hog production houses (Childers et al., 2001), waste storage and treatment lagoons (Aneja et al., 2000), land application of lagoon slurry to adjacent cropland (Sommer, 1997), and subsequent reemission of ammonia from the soil (Roelle and Aneja, 2001).

Effects of Ammonia

Over the past decade, agricultural ammonia emissions have attracted attention in the state of North Carolina due to the explosive growth of its hog population and associated facilities. Enhanced ammonia emissions can promote detrimental environmental processes including particulate matter formation and aquatic eutrophication. Measurements made at a typical swine facility in eastern North Carolina suggest that gaseous ammonia concentrations exceed average ambient levels and that ammonium aerosols dominate the fraction of fine particle matter near agricultural

ammonia sources (McCulloch et al., 1998). Ammonia reacts readily with water or acidic species in the atmosphere to form ammonium ions or ammonium aerosols. Through these reactions, ammonia affects the composition and pH of precipitation (Warneck, 2000), cloudwater (Kim and Aneja, 1992) and atmospheric aerosols (Lefer et al., 1999). In creating ammonium aerosols, ammonia enhances the light extinction capability of atmospheric compounds, leading to a decrease in visibility. Gaseous ammonia quickly undergoes dry deposition, with deposition velocities ranging up to 2 cm/s (Hanson and Lindberg, 1991). Due to its high deposition velocity and its reactivity in the atmosphere, gaseous ammonia has a relatively short atmospheric lifetime, on the order of a few days or less (Warneck, 2000). Ammonium aerosol deposits more slowly than gaseous ammonia, with a deposition velocity of roughly 0.2 cm/s (Warneck, 2000). Therefore it has a longer atmospheric lifetime than gaseous ammonia, on the order of 1 to 15 days (Aneja et al., 1998), and a more extensive spatial sphere of influence.

Measurements made at National Atmospheric Deposition Program/National Trends Network sites in North Carolina illustrate an increasing trend in ammonium concentration in precipitation since 1990 (Walker et al., 2000). This trend occurs in conjunction with an increase in the number of nearby swine operations. Furthermore, air mass trajectories directly correlate agricultural ammonia emissions with the enhanced ammonium concentration in precipitation. Air mass trajectories also suggest that wet deposition of ammonia and ammonium emitted from agricultural operations in eastern North Carolina could potentially affect all river basins in the Coastal Plain Region, as well as sensitive coastal ecosystems and estuaries (Walker et al., 2000).

Excessive nutrient loading in aquatic ecosystems creates a condition of accelerated primary productivity or eutrophication. Deposition of atmospheric nitrogen accounts for approximately 10% of the nitrogen loading that occurs in waters adjacent to non-industrialized regions, and it contributes up to 50% of the nitrogen loading that occurs in waters downwind of industrialized or intensively farmed regions (Paerl, 1995). Estuaries, coastal and continental shelf regions account for up to one half of the world's oceanic primary production, yet they encompass only 15% of the surface area of the world's oceans. Enhanced nutrient loading in coastal waters accounts for part of this relatively large fraction of oceanic production. Over the past few decades, excessive nitrogen loading has caused an increase in toxic and non-toxic phytoplankton blooms in these sensitive nitrogen-limited ecosystems (Paerl, 1995). In North Carolina, atmospheric deposition of nitrogen compounds accounts for an estimated 38% of the nitrogen loading that occurs in the Neuse River-Pamlico Sound (Paerl and Fogel, 1994). Ammonia emissions from extensive commercial hog operations potentially provide a large portion of the atmospheric nitrogen compounds that deposit and contribute to nitrogen loading in North Carolina's sensitive aquatic ecosystems (Paerl, 1997). Due to such environmental effects as aquatic eutrophication and particulate matter formation, ammonia and other pollutant emissions from commercial hog operations located in eastern North Carolina have recently garnered much attention.

Quantification of Sources

Reductions in ammonia emissions can mitigate some of the negative effects of atmospheric ammonia. However, before reduction strategies are determined or implemented, scientists must first quantitatively assess the various sources and deposition

processes of gaseous ammonia and ammonium aerosol. Through a combination of field measurements and theoretical modeling, scientists have investigated ammonia emissions associated with agricultural activities in order to determine appropriate emission factors. Traditionally in North Carolina, commercial hog operations utilize lagoon and spray technology for waste treatment. In this type of system, the waste is broken down and stored in primary, secondary and tertiary anaerobic waste treatment lagoons and is ultimately sprayed on adjacent crop land as fertilizer. Measurements of ammonia flux from hog waste treatment lagoons (Aneja et al., 2001a; Aneja et al., 2000) and from fertilized and unfertilized soils (Roelle and Aneja, 2001) have been collected and analyzed with respect to corresponding environmental parameters, including lagoon and soil temperature, pH, and the concentration of ammonia and ammonium in the waste lagoons, called Total Ammoniacal Nitrogen (TAN) (Table 1.2).

This study presents ammonia flux measurements made from experimental waste treatment and storage technologies at three swine facilities located in central and eastern North Carolina, namely Barham Farm, Grinnels Laboratory, and Howard Farm. Specifically, the results include ammonia flux measurements made from alternative waste treatment lagoon systems at Barham Farm and Howard Farm, from cropland soils at Howard Farm, from the cover of an in-ground anaerobic waste digester at Barham Farm, and from a conveyor belt system located within a hog housing unit at Grinnels Laboratory. Ammonia flux measurements made from the liquid waste components of Barham Farm's and Howard Farm's systems are evaluated with respect to ammonia flux measurements made from traditional waste treatment lagoons. Ammonia flux measurements made from the experimental waste treatment lagoon systems are also

parameterized with respect to corresponding environmental parameters, including air temperature, effluent temperature, effluent pH, and effluent TAN concentration.

The field measurement campaigns included in this study are part of the Odor, Pathogens, and Emissions of Nitrogen (OPEN) Program run by North Carolina State University's Animal and Waste Poultry Management Center. Program OPEN involves 18 swine operations in eastern North Carolina, each of which utilizes an experimental waste treatment technology which is potentially environmentally superior in comparison with traditional waste treatment technologies. Program OPEN scientists quantitatively investigate each farm in order to determine whether its waste treatment technology emits relatively lower concentrations of odor, pathogens, ammonia and other nitrogen compounds in comparison to the traditional lagoon and spray technology.

Previous studies have investigated theoretical models that describe the flux of ammonia from domestic animal waste. Jayaweera and Mikkelsen (1990) have constructed a model to predict ammonia volatilization from flooded soil systems that incorporates TAN, pH, temperature, floodwater depth and wind speed. Ammonia volatilization from manure pits in swine buildings has also been investigated. The model established for this process relies on parameters such as manure temperature and air velocity (Zhang et al., 1994). Westerman et al. (1999) have created a model for ammonia flux from anaerobic swine waste lagoons that takes into account liquid pH, temperature, wind speed and TAN. De Visscher et al. (2002) have expanded on that two layer model. The model accounts for the aqueous equilibrium reaction of ammonia and ammonium, the adsorption of ammonium on suspended organic material, and the diffusive transfer of ammonia and ammonium across liquid and air boundary layers. The model incorporates

effluent concentration, water temperature, wind speed, and effluent pH. The model simulates ammonia emissions measured via micrometeorological techniques (Harper and Sharpe, 1998) and explains 70% of the variation observed in daily averaged ammonia flux measurements (De Visscher et al., 2002).

Aneja et al. (2001b) have developed a coupled mass transfer with chemical reactions model that describes ammonia flux across a swine waste lagoon-air interface. This two layer model takes into account the equilibrium reaction of ammonia and ammonium in aqueous, the pseudo-first order reaction of ammonia with water and acidic species in the atmosphere, and the molecular transfer of ammonia across liquid and gas films on either side of the interface. The coupled model incorporates air temperature, lagoon temperature, lagoon pH, wind speed, TAN, and ambient ammonia concentration, all of which are monitored during field campaigns. The modeled ammonia flux exhibits an exponential increase with lagoon temperature and pH and approximately linear increases with wind speed and TAN (Aneja et al., 2001b).

This study includes a comparison of ammonia flux measurements made at the two experimental waste treatment lagoon systems and ammonia flux measurements made at traditional hog waste lagoons with corresponding modeled ammonia flux calculated using the coupled mass transfer with chemical reactions model (Aneja et al., 2001b) and environmental data collected during ammonia flux measurement periods. Parameters measured continuously during ammonia flux measurement periods are input into the model to facilitate this comparative analysis. By simultaneously evaluating modeled and measured ammonia flux with respect to corresponding environmental parameters, discrepancies can be established and analyzed, highlighting characteristics of the model

or the measurements that require attention. In this manner, this study strives to quantitatively assess ammonia flux from alternative and traditional hog waste treatment technologies via a combination of modeling and measurements in order to advance the development of emission reduction strategies and sustainable agricultural operations.

Field Measurements

Dynamic Flow-Through Chamber System

A dynamic flow-through chamber system (Aneja et al., 2000; Chauhan, 1999; Aneja et al., 1996; Kim et al., 1994; Kaplan et al., 1988) is used to measure ammonia flux from various surfaces. This study includes ammonia flux measurements made over liquid waste surfaces (Figure 1.6), cropland soil surfaces, and the surface of the cover of an in-ground anaerobic waste digester. The liquid waste surfaces in the present study include constructed wetland cells and waste lagoons that have recently been converted to waste storage ponds. Measurements over traditional hog waste treatment lagoons have been made in previous studies (Aneja et al., 2001a; Aneja et al., 2000).

For liquid waste surfaces, the system consists of a four foot by four foot floating plywood platform and a plastic cylindrical chamber. Foam board and a frame of PVC piping support the floating platform. The translucent chamber fits into a circular hole cut in the center of the platform and penetrates the lagoon surface by approximately 8 cm. A circular plastic cover bolted to the top of the cylinder and the seal formed between the bottom of the cylinder and the lagoon water form a closed system inside the chamber. For solid surfaces, such as the cropland soil surfaces and the cover of the in-ground anaerobic waste digester, the chamber fits into a stainless steel ring rather than into a floating platform. The stainless steel ring is driven into the ground or secured to the

digester cover in order to form a sealed system. Fluorinated ethylene propylene (FEP) Teflon lines the entire inner surface of the chamber. The chamber has a diameter of 25.4 cm, an internal height of 45.72 cm, and a volume of 23,167 cm³.

A carrier gas of compressed air travels into the chamber through ¼ inch Teflon lines at a constant flow rate set by a mass flow controller and monitored by a datalogger. The carrier gas transports the sample air stream to the ammonia analyzer. A variable speed motor mounted on the top of the chamber runs a Teflon impeller stirrer in the chamber in order to keep the air inside well mixed. The sample from the chamber travels to the detection instruments through ¼ inch Teflon tubing. The closed system utilizes Teflon tubing, Teflon lining, and stainless steel fittings in order to minimize chemical reactions with the sample stream. The Teflon tubing has an inner diameter of 0.3 cm, and the Teflon lines stretch approximately 10 m in length. With an average flow rate of 5 lpm, this equates to a sample residence time of approximately 5 minutes in the system and 3 seconds in the lines at steady state. A vent on the sample line exiting the chamber prevents the system from over pressurizing. The vent is periodically bubble tested during sampling periods in order to check for under pressurization and leaks in the system.

Sampling Scheme

For ammonia flux measurements made using the dynamic chamber system, sampling consists of measuring the gaseous ammonia concentration of the sample stream exiting the dynamic chamber system on a continuous basis. Simultaneous measurements of ambient ammonia, effluent temperature, effluent pH, air temperature, relative humidity, wind speed, wind direction, and solar radiation also occur. One to three samples of waste water taken adjacent to the floating platform are collected each day

during ammonia flux measurement periods in order to determine the concentration of TAN in the liquid effluent. On a daily basis, sampling begins as early in the morning as possible, from 7:00 AM to 10:00 AM. Sampling ends from 5:00 PM to 7:00 PM, or continues overnight in order to attain a diurnal profile.

In order to perform sampling over liquid waste surfaces, the chamber is bolted to the floating platform, and the entire system is set afloat on the lagoon. A 3 m PVC pipe and two 7.5 m ropes secure the platform to the shore and anchor the floating platform in place. The sample lines and the lines from the sensors and the motor on the platform run through the PVC pipe in order to avoid contact with the lagoon. The platform is placed as far from the edge of the lagoon as possible, in order to minimize any boundary effects. For sampling over solid surfaces, the stainless steel ring is driven into the ground, and the chamber is inserted into the stainless steel ring a few hours prior to sampling.

Before each daily or diurnal sampling period, the chamber system is flushed with compressed air in order to dissipate any accumulated moisture or ammonia in the system and also to ensure that the ammonia analyzers measure steady state ammonia concentration from the sample stream. Between each daily or diurnal sampling period, the floating chamber system is moved in a stratified statistically random manner to another location on the lagoon within a 10 m radius of the mobile laboratory. In order to capture the various subsections of each farm's waste treatment system, the mobile laboratory, meteorological tower, and floating chamber system must be periodically moved. The ammonia analyzers are calibrated before sampling begins at each new subsection. Each field campaign lasts for approximately two weeks.

In order to quantify ammonia emissions from hog houses, such as the alternative waste treatment technology located within the hog housing unit at Grinnels Laboratory, continuous measurements of ammonia concentration are taken from the stream of air exiting the house vent. The ammonia flux from the housing unit equals the ammonia concentration of the sample stream multiplied by the average velocity of air exiting the vent.

Chamber Effects

As with any environmental investigation that involves imposing a constructed system on the natural environment, concerns arise in response to the use of the dynamic chamber system. Sensitivity investigations can elucidate the extent to which an experimental system alters the ambient conditions of the associated microclimate. For a dynamic chamber system such as the one used in this study, temperature and humidity experiments address the concern that the chamber creates a “greenhouse effect”. The lagoon temperature both inside and outside the chamber are continuously monitored and exhibit an average difference 0.39 ± 1.48 °C during ammonia flux measurement periods. The air temperatures inside and outside the chamber have been measured while monitoring ammonia flux over the covered lagoon at Barham Farm and exhibit an average difference of 1.55 ± 2.30 °C. In order to quantify the effect of excessive humidity or moisture in the dynamic chamber system, Roelle (2001) has introduced visible moisture droplets on the chamber walls and reports ammonia losses ranging from 6 to 7%. In the present study, with compressed air as a carrier gas, humidity may accumulate within the chamber. However, the flow of air through the chamber system consistently inhibits any visible moisture droplets from forming during measurement periods. Thus,

ammonia losses due to moisture in the chamber lie well within the constraints of the humidity experiment and are therefore determined to be minimal.

The dynamic chamber system performs as a Continuously Stirred Tank Reactor (CSTR). The air within the chamber is considered ideally mixed, meaning that all elemental units of air within the chamber have the same composition. Trace experiments testing the flow and mixing characteristics of this type of system have indicated that negligible stagnancy or channeling occurs within the chamber (Aneja, 1976). The vent on the sample line exiting the chamber minimizes the pressure difference between the ambient atmosphere and the air inside of the chamber.

In order to assess the effect of mixing speed on calculated ammonia flux, the impeller stirrer speed has been varied between 20 rpm and 60 rpm during the afternoon of a typical diurnal sampling period. Fluctuations in ammonia flux observed during this experiment are consistent with the typical diurnal variation of ammonia flux. No statistically significant differences in calculated ammonia fluxes are observed in conjunction with a change in impeller speed from 20 rpm to 40 rpm or from 40 rpm to 60 rpm. Thus, varying the impeller speed by 20 rpm or less does not seem to affect the calculated ammonia flux to a significant extent. However, a statistically significant decrease in average calculated flux does occur in conjunction with a decrease in impeller speed from 60 to 20 rpm. The difference is not consistent with the normal diurnal pattern of ammonia flux. Since a larger change in impeller speed seems to affect the calculated ammonia flux to a significant extent, the impeller speed is kept between 40 and 60 rpm during the ammonia flux sampling periods included in this study.

In order to ascertain the relation between wind speed inside and outside the chamber, the velocity of air within the chamber has been compared to the horizontal wind speed just above the lagoon surface. While establishing equality of wind speeds inside and outside the chamber by no means establishes equality of ammonia emissions inside and outside the chamber, the insight gained by this comparison can be used to extend empirical and theoretical investigations of ammonia emission. Wind speed at a height of approximately 10 m is continuously monitored during ammonia flux measurement periods. Using the power law profile (Arya, 1999) the corresponding wind speeds at a height of 0.5 m are calculated. Equation 1.1 describes the power law profile.

$$\frac{V}{V_r} = \left(\frac{z}{z_r} \right)^m \quad (1.1)$$

V_r and Z_r are the reference wind velocity and reference height; m equals 0.1 for a smooth surface in unstable daytime conditions, and V is the wind velocity at height z . The power law profile is only applied to wind speeds measured during daytime hours, for using 0.1 as the exponent for the power law is only appropriate during unstable daytime conditions (Arya, 1988). The ten meter wind speeds range from 0.00 m/s to 6.40 m/s, while the calculated 0.5 m wind speeds range from 0.00 m/s to 4.75 m/s.

In order to estimate wind speeds within the chamber, the air flow velocity within the chamber at various carrier gas flow rates and impeller speeds have been measured by a digital hot wire anemometer. In this manner, relationships between the carrier gas flow rate and the flow speed within the chamber, referred to as chamber wind speed, at impeller speeds of 40 rpm and 60 rpm have been determined (Figure 1.7). Chamber wind speeds are then calculated using the observational relationships and the carrier gas flow rate data, which is logged continuously during measurement periods. The calculated

chamber wind speeds range from 0.95 m/s to 1.93 m/s and are less variable than wind speeds outside the chamber, for the flow rate of the carrier gas remains relatively stable. The chamber wind speeds fall within the range of wind speeds estimated outside the chamber at a height of 0.5 m.

To as great an extent as possible within the scope of this study, the effects of imposing a dynamic chamber system on a natural environment have been investigated. More extensive examination of the relationship between impeller speed, carrier gas flow rate and chamber wind speed would reveal more definitive conclusions and would instigate improvements to the current system.

Ammonia Analyzers

Thermo Environmental Instruments Incorporated (TECO) Model 17c chemiluminescence ammonia analyzers continuously monitor ammonia concentration during ammonia flux measurement periods. The theory of the instrument relies on the gas phase reaction between ozone (O₃) and nitric oxide (NO), as illustrated in Equation 1.2.



The photons emitted in this reaction are proportional to the concentration of nitric oxide. A photomultiplier tube detects the photons and translates this reading into a nitric oxide concentration after calibration with known standards (TECO, 1999).

In order to quantify ammonia, the sample stream entering the analyzer separates into three parts (Figure 1.8). In the first flow path, the sample mixes with ozone, and all of the nitric oxide reacts to produce a reading of nitric oxide concentration. In the second flow path, the sample passes through a molybdenum converter (325°C) which converts all

oxidized forms of nitrogen to nitric oxide. The converted sample then reacts with ozone in order to quantify the concentration of all nitrogen oxides (NO_y). In the third flow path, a stainless steel converter (750°C) converts all nitrogen oxides and ammonia into nitric oxide, which results in a reading of total nitrogen (N_T). The sample stream alternates between the three flow paths. The ammonia concentration equals the difference between the total nitrogen signal and the signal from the oxides of nitrogen, as illustrated in Equation 1.3 (TECO, 1999).

$$[\text{NH}_3] = [\text{N}_T] - [\text{NO}_y] \quad (1.3)$$

During field campaigns, the ammonia analyzers are located in a mobile laboratory contained within a modified Ford Aerostar van. The analyzers operate effectively within a certain temperature range. Therefore, a 13,500 BTU air conditioning unit regulates the climate in mobile laboratory.

Environmental Parameters

During ammonia flux experiments, two Campbell Scientific Instruments 107 Temperature Probes measure effluent temperature, and an Innovative Sensors pH probe monitors effluent pH adjacent to the chamber. One of the lagoon temperature probes and the pH probe hang off the edge of the wooden platform and are submerged under the lagoon water by approximately 15 cm. The other effluent temperature probe is fastened to the underside of the platform and monitors effluent temperature inside the chamber. A meteorological tower containing a Campbell Scientific Instruments CS500 temperature and relative humidity probe, a LI-Cor 200SZ pyranometer, and a Campbell Scientific Instruments Met One 034A-LC Windset integrated cup anemometer and wind vane

measure the ambient air temperature, relative humidity, solar radiation, wind speed, and wind direction.

Up to three samples of waste water are taken daily and are analyzed for TAN concentration by the Biological and Agricultural Engineering Department at North Carolina State University. Waste water analysis occurs in the Weaver Laboratory via colorimetric analysis with a sodium base reagent. The pH of the waste water samples is also measured during laboratory analysis. Ambient ammonia concentration is monitored continuously by one of the Model 17c chemiluminescence ammonia analyzers. A sample stream of ambient air travels through ¼ inch Teflon tubing from the top of the 10 m meteorological tower to one of the ammonia analyzers housed in the mobile laboratory.

Instrument Calibration

Calibration of the ammonia analyzers is performed using certified standard mixtures of nitric oxide and ammonia, zero grade air, and a Thermo Environmental Instruments 146 dilution/titration instrument. The calibration instrument is periodically serviced and calibrated to specifications by the manufacturer. The 146 calibrator mixes the appropriate gas standard with zero grade air in order to deliver a known concentration of nitric oxide or ammonia to the analyzers. Nitric oxide is used to calibrate the oxidized nitrogen and total nitrogen channels, whereas ammonia is used to calibrate the ammonia channel.

A multipoint calibration typically consists of points at zero, 80%, 60%, 40%, and 20% of the full scale range. The full scale range typically equals 20 ppm for liquid waste surface measurements and 0.5 ppm for soil surface measurements. A multipoint calibration of the ammonia analyzers is conducted prior to each measurement campaign.

Zero and span checks occur approximately every other day during the campaign, and the multipoint calibration is rechecked at the conclusion of each measurement period. The Innovative Sensors pH probe is calibrated using standard buffer solutions of pH 4.00±0.01, 7.00±0.01, and 10.00±0.02, and the Campbell Scientific liquid waste and air temperature probes are periodically checked using a Fisherbrand Traceable Alarm Thermometer.

Data Acquisition System

A Campbell Scientific Instruments 21X Micrologger located in the mobile laboratory logs the data from all ambient sensors and the ammonia analyzers. The datalogger continuously records a signal from each instrument every second. The datalogger is programmed to average, record, and store measurements from all sensors every fifteen minutes. Therefore, every data point collected represents an average of 900 signals processed by the datalogger. The logged data is downloaded and checked on a daily basis.

Ammonia Flux Calculation

The following mass balance expression (Equation 1.4) describes the chemical and physical dynamics within the flow-through chamber system used to quantify ammonia flux for this study.

$$\frac{dC}{dt} = \left[\frac{qC_o}{V} + \frac{JA}{V} \right] - \left[\frac{LA_w}{V} + \frac{LA}{V} + \frac{q}{V} \right] (C) - R \quad (1.4)$$

where

J = ammonia flux in dimensions of mass per area per time

C = ammonia concentration within the chamber

C_o = ammonia concentration at the chamber inlet

q = flow rate of compressed air through the chamber

V = volume of the chamber above the surface

A = cross sectional area of the top and bottom of the chamber

A_w = surface area of the inner walls of the chamber above the surface

L = ammonia loss due to reaction with inner surfaces of the chamber

R = chemical production/destruction rate in the gas phase within the system

Because the chamber is well mixed, the concentration of ammonia in the chamber, C , remains uniform throughout the chamber and the sample lines leading from the chamber to the ammonia analyzer. Therefore, the ammonia analyzer measures the ammonia concentration within the chamber. Using compressed air as a carrier gas, the initial concentration of ammonia at the inlet of the chamber is negligible. Due to the short residence time of the sample stream within the chamber system and the use of compressed air as a carrier gas, the gaseous ammonia emitted from the surface does not chemically react to a significant extent, so R is also negligible. As the system approaches equilibrium, the instantaneous change in ammonia concentration with time approaches zero. Therefore, at steady state dC/dt equals zero. These conditions lead to the following equation for ammonia flux at steady state (Equation 1.5).

$$J = \left[(L) \left(\frac{2}{r} + \frac{1}{h} \right) + \frac{q}{V} \right] (C)(h) \quad (1.5)$$

r and h denote the radius and height of the chamber, and the other variables have been defined. The flow rate, chamber dimensions and steady state ammonia concentration are measured, while the loss term is determined experimentally. Based on the method of Kaplan et al. (1988), the loss term depends on the slope of the plot of

$-\ln\left[\frac{C_{eq} - C(t)}{C_{eq} - C_o}\right]$ versus time (t). For this experiment, C_o equals the ammonia

concentration measured from the chamber system after it reaches an initial equilibrium state with a constant carrier gas flow rate. C_{eq} equals the concentration of ammonia measured from the chamber system once it has reached a second equilibrium state at a lower carrier gas flow rate. $C(t)$ represents the concentration of ammonia at any time, t , during the transition between the two equilibrium states. L depends on the slope of the best fit line through the points of the plot, as illustrated in Equation 1.6

$$L = \left[\frac{\left(Slope - \frac{q}{V} \right)}{\left(\frac{2}{r} + \frac{1}{h} \right)} \right] \quad (1.6)$$

L has dimensions of length per time. The loss term calculated for this study equals 0.01723 m/min and represents the average result from four loss term experiments that took place at different times throughout the ammonia flux measurement periods.

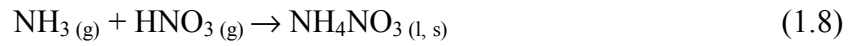
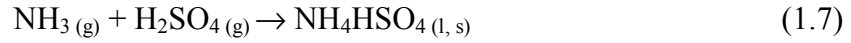
Modeling Exercise

A coupled mass transfer with chemical reactions model (Aneja et al., 2001b; Malik, 1999) for ammonia flux across a gas-liquid interface simulates ammonia flux measurements from hog waste treatment lagoons made in this study and in previous studies (Aneja et al., 2001a; Aneja et al., 2000). The lagoon temperature, air temperature, lagoon pH, lagoon TAN, wind speed, and ambient ammonia monitored during field campaigns are input into the model, resulting in an output of ammonia flux. Based on the quiescent thin film concept (Danckwerts, 1970), the model includes a thin gas film extending from the air-liquid interface to the well-mixed region of the air and a thin

liquid film extending from the air-liquid interface to the well-mixed region of the liquid (Figure 1.9). The well-mixed regions of air and liquid are referred to as the bulk gas and liquid phases and are assumed to be of indeterminate height. Molecular diffusion and chemical reactions are accounted for as transport mechanisms in both films.

Gas Phase Dynamics

The model includes the gas phase chemical reactions of ammonia with sulfuric acid, nitric acid, hydrochloric acid, and the hydroxyl radical (OH•), illustrated in the following equations.



The following basic diffusion equation governs the concentration gradient of ammonia in the gas film (Equation 1.11).

$$D_a \left(\frac{d^2 C}{dz^2} \right) = K_a (C) \quad (1.11)$$

D_a represents the diffusivity of ammonia in the gas phase. K_a equals the pseudo first order reaction rate of ammonia in the gas phase, calculated by assuming constant concentrations of sulfuric acid, nitric acid, hydrochloric acid, and the hydroxyl radical (Malik, 1999). C represents the concentration of gaseous ammonia at height z .

The solution to the basic diffusion equation using the following boundary conditions (Equation 1.12) describes the concentration of ammonia with respect to height within the gas film.

$$\begin{aligned} z = 0; C(0) &= C_{ai} \\ z = t_a; C(t_a) &= C_a \end{aligned} \quad (1.12)$$

The flux of ammonia to the atmosphere is proportional to the negative ammonia concentration gradient in the gas film. The resulting equation for ammonia flux to the atmosphere is as follows (Equation 1.13).

$$J_a = \left\{ \frac{-D_a r_a}{A - (1/A)} \right\} \left\{ (C_a - C_{ai}(1/A))e^{r_a z} - (C_{ai}A - C_a)e^{-r_a z} \right\} \quad (1.13)$$

In the above equation, J_a represents the ammonia flux to the atmosphere across the gas film. A represents $e^{r_a t_a}$, in which r_a equals $\sqrt{K_a/D_a}$ and t_a equals the thickness of the gas film. C_a and C_{ai} represent the concentration of ammonia in the bulk gas phase and at the air-liquid interface, respectively. The thickness of the gas film is defined as the ratio of the gas phase diffusion coefficient of ammonia to the gas phase mass transfer coefficient of ammonia, determined experimentally by Mackay and Yeun (1983). The thickness of the gas film ultimately relies on wind speed and the viscosity, density, and temperature of the air.

Liquid Phase Dynamics

The equilibrium reaction of ammonia and ammonium dictates the transport of ammonia in the liquid film (Equation 1.14).



The following component material balance (Equation 1.15) underlies the dynamics of the model in the liquid film. It encompasses molecular transport within the liquid film and corresponds to the liquid phase equilibrium reaction between ammonia and ammonium (Olander, 1960).

$$D_L \left(\frac{d^2 C_L}{dz^2} \right) + D_L' \left(\frac{d^2 C_L'}{dz^2} \right) = 0 \quad (1.15)$$

D_L and C_L represent the diffusivity and concentration of ammonia, and D_L' and C_L' represent the diffusivity and concentration of ammonium. The concentrations of ammonia and ammonium in the liquid phase depend on the lagoon pH and TAN concentration, while the liquid phase diffusivities of ammonia and ammonium depend on temperature and viscosity.

The solution to the component material balance equation describes the concentration of ammonia with respect to height in the liquid film. The flux of ammonia to the liquid is proportional to the negative ammonia concentration gradient in the liquid film. Olander (1960) has applied the following boundary conditions (Equation 1.16) in order to define the expression for ammonia flux to the liquid film.

$$\begin{aligned} z = 0; C(0) &= C_{Li} \\ z = t_L; C(t_L) &= C_L \end{aligned} \quad (1.16)$$

The resulting equation for ammonia flux to the liquid film is as follows (Equation 1.17).

$$J_L = \left(\frac{D_L}{t_L} \right) (C_{Li} - C_L) \left(1 + (D_L' / D_L) K \right) \quad (1.17)$$

J_L denotes the flux of ammonia to the liquid film. C_{Li} and C_L equal the concentration of ammonia at the air-liquid interface and in the bulk liquid phase, respectively. C_L is based on the TAN concentration of the liquid. K equals the ratio of ammonium concentration to ammonia concentration, which depends on the equilibrium reaction rate (Zhang et al., 1998) and the pH of the liquid. t_L represents the thickness of the liquid film, which equals the ratio of the diffusivity of ammonia to the mass transfer coefficient of ammonia in the liquid phase (Mackay and Yeun, 1983). Similar to the thickness of the gas film,

the thickness of the liquid film ultimately relies on wind speed and the viscosity, density and temperature of the liquid.

Net Ammonia Flux

At the interface, the ammonia flux to the gas phase equals the negative of the ammonia flux to the liquid phase. Henry's Law relates the equilibrium gas and liquid phase concentrations of ammonia at the interface (Equation 1.18).

$$HC_{Li} = C_{ai} \quad (1.18)$$

H equals the Henry's Law constant for ammonia, as defined by Dasgupta and Dong (1986). C_{Li} and C_{ai} are the concentrations of ammonia in the liquid and gas phases at the interface, respectively. By setting the ammonia flux to the gas phase equal to the negative ammonia flux to the liquid phase and by utilizing Henry's Law, an expression for net ammonia flux across the interface is obtained (Equation 1.19).

$$J = \frac{(D_a r_a) \{ HC_L (A + 1/A) - 2C_a \}}{(A - 1/A) \{ 1 + H(A + 1/A)(B) \}} \quad (1.19)$$

In which

$$B = \frac{D_a r_a t_L}{D_L (A - (1/A)) (1 + (D'_L / D_L) K)} \quad (1.20)$$

J equals the net flux of ammonia across the gas-liquid interface and has dimensions of mass per area per time. The other variables have been defined. The net ammonia flux output by the coupled model describes the flux of ammonia to the atmosphere across the surface of a waste treatment lagoon. In the model, ammonia flux ultimately depends on lagoon temperature, lagoon pH, wind speed, lagoon TAN concentration, air temperature and ambient ammonia concentration. Measurements of these parameters occur in conjunction with ammonia flux measurements during field campaigns. Thus, measured

ammonia fluxes may be compared to corresponding ammonia fluxes output by the coupled model.

Summary of Objectives

- 1) Measure ammonia emissions from experimental hog waste treatment technologies at swine facilities located in eastern North Carolina.
- 2) Evaluate ammonia emissions from the liquid waste components of the experimental waste management systems with respect to ammonia emissions from traditional hog waste treatment lagoons.
- 3) Develop an observational model relating ammonia flux from the liquid waste components of the experimental waste management systems to environmental parameters such as effluent temperature, pH and TAN concentration.
- 4) Validate the mechanistic coupled mass transfer with chemical reactions model (Aneja et al., 2001b) with ammonia flux measurements from experimental and traditional hog waste treatment lagoons.
- 5) Evaluate the observational and mechanistic models with respect to field data.

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Table 1.1 Estimates of Global Ammonia Sources (10^{12} g N/yr) (Warneck, 2000).

Process	Warneck (1988)	Schlesinger and Hartley (1992)	Dentener and Crutzen (1994)
Automobiles	0.2	0.2	---
Biomass Burning	2-8	5	2
Coal Combustion	≤ 2	2	---
Domestic Animals	22	32	22
Fertilizer Losses	3	9	6.4
Human Excrements	3	4	---
Oceans	---	13	7
Soils/Plant Emissions	15	10	5.1
Wild Animals	4	---	2.5
Approximate Sum of Sources	54	75	45

Table 1.2 Ammonia Flux Measurements from Hog Waste Lagoons in North Carolina (Aneja et al., 2001a; Aneja et al., 2000).

Site	Date	Mean Ammonia Flux $\mu\text{gNH}_3\text{-N/m}^2\text{/min}$	Mean Lagoon Temperature $^{\circ}\text{C}$	Mean Lagoon pH	TAN mgN/L
Sampson County, NC	August 1997	4,017	30.0	7.50	550.9
Sampson County, NC	December 1997	844	11.6	8.00	563.8
Sampson County, NC	February 1998	305	12.1	7.80	545.4
Sampson County, NC	May 1998	1,706	24.7	7.70	512.8
Raleigh, NC	September 1998	80	23.3	7.78	104.8
Raleigh, NC	October 1998	58	20.1	6.94	41.5
Rocky Mount, NC	Early November 1998	41	12.0	7.41	298.8
Rocky Mount, NC	Late November 1998	51	12.5	7.04	350.0
Kenansville, NC	Early March 1999	120	10.3	7.33	550.0
Warsaw, NC	Late March 1999	108	17.8	6.82	786.8

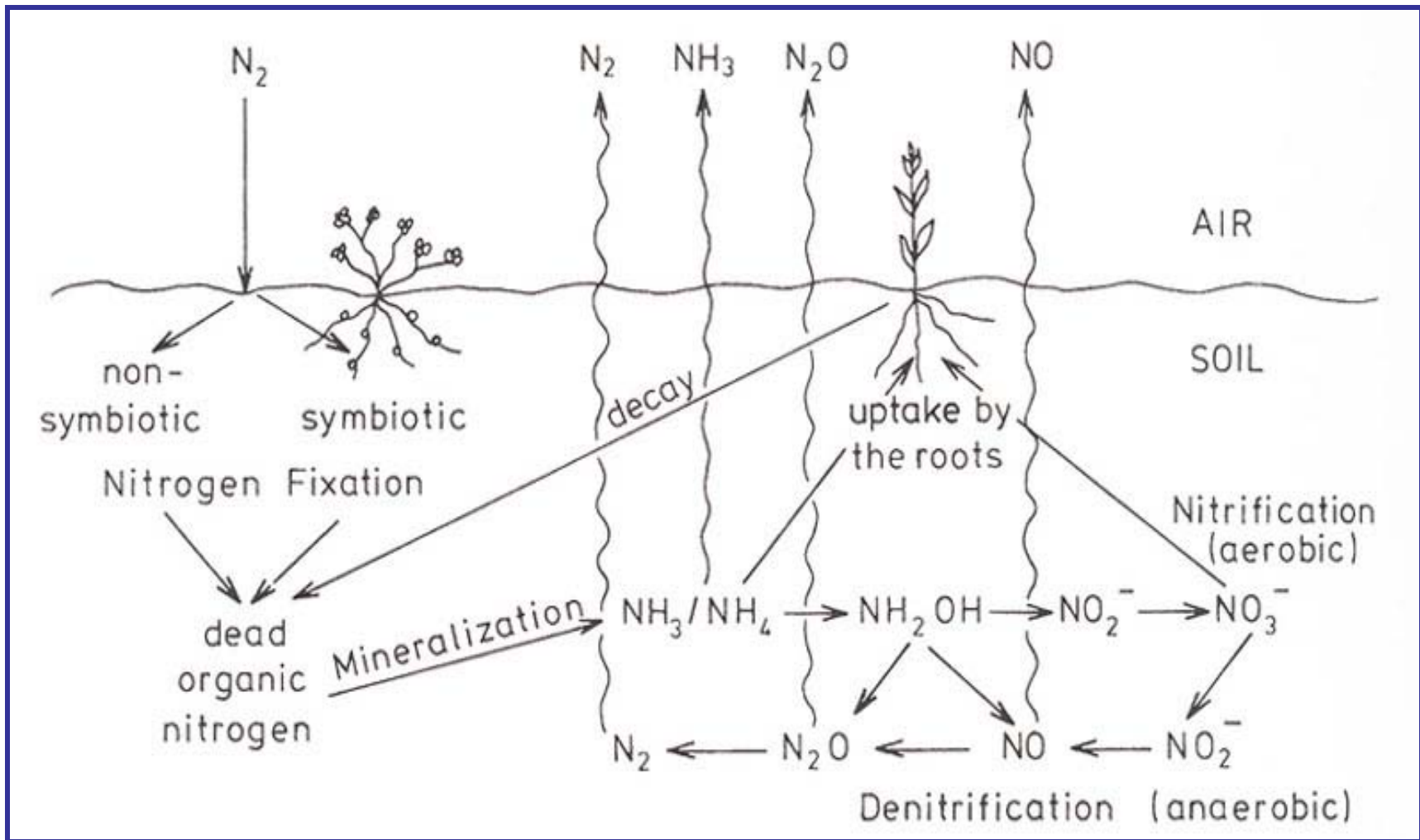


Figure 1.1 Biological Nitrogen Cycle (Warneck, 2000).

North Carolina Swine Population

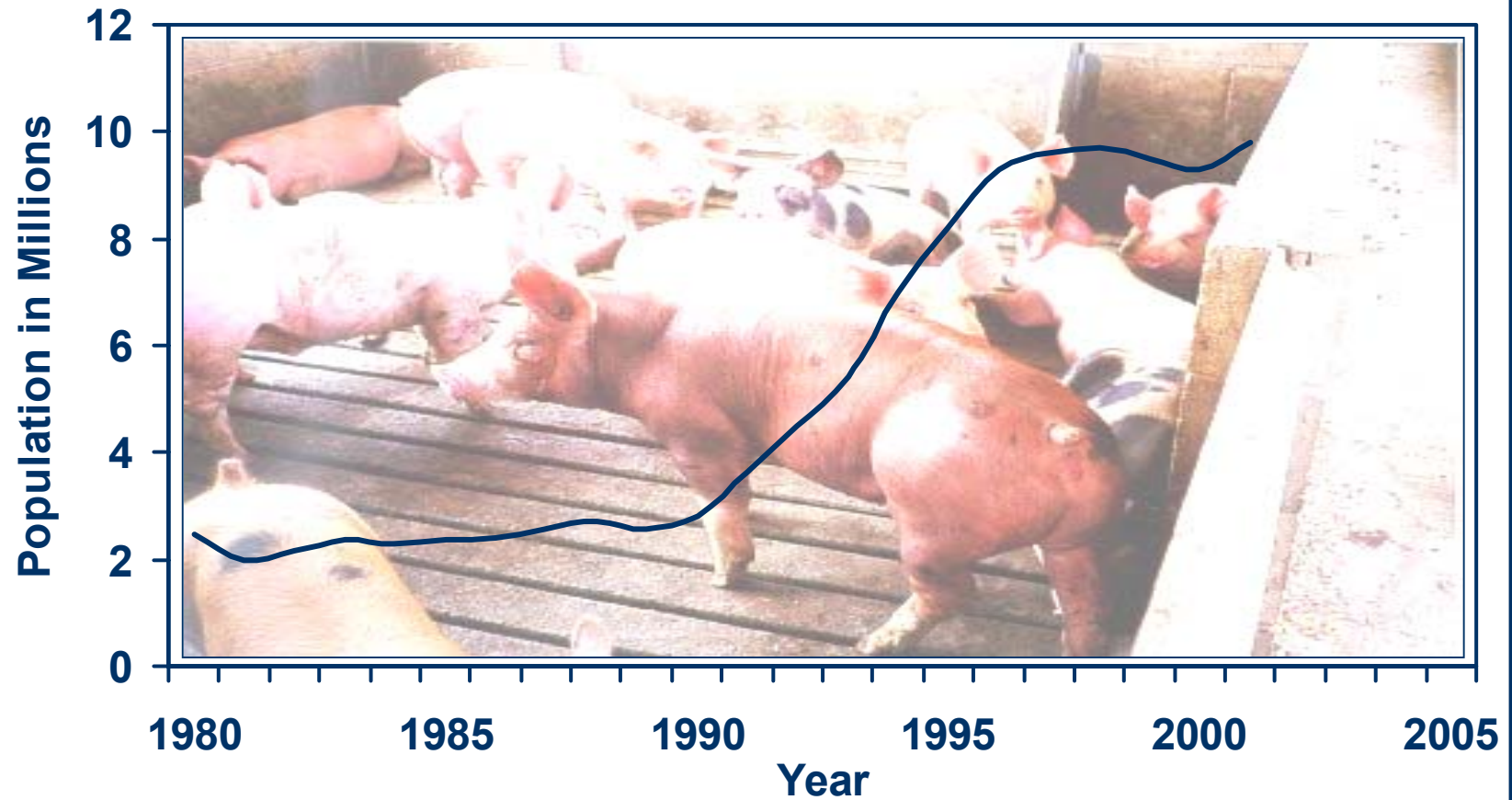


Figure 1.2 Swine Population in North Carolina (NCDA&CS, 2002).

North Carolina Coastal Plain Region Swine Population

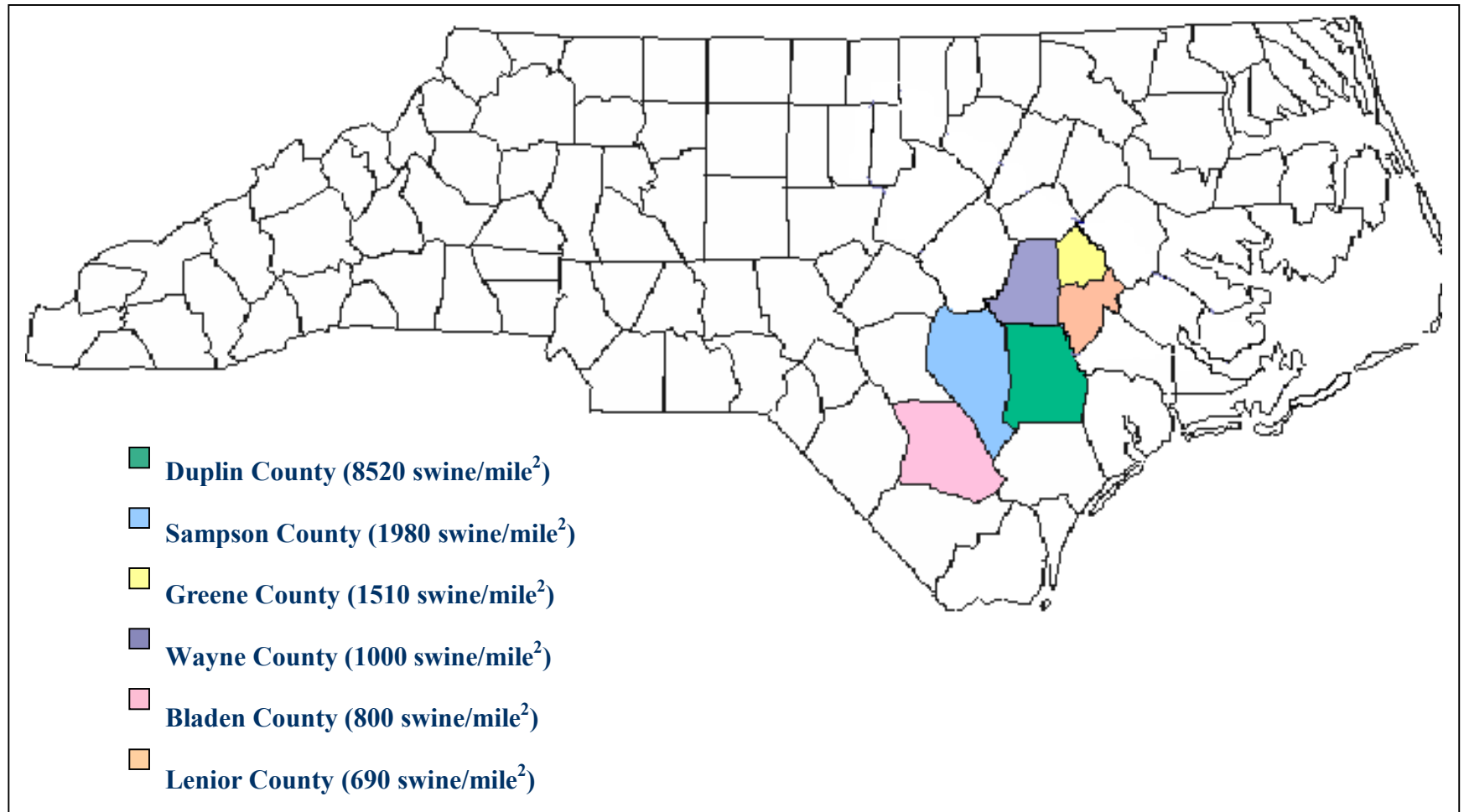


Figure 1.3 Six Counties with High Swine Densities in North Carolina (NCDA&CS, 2002).

Sources of Atmospheric Nitrogen in North Carolina

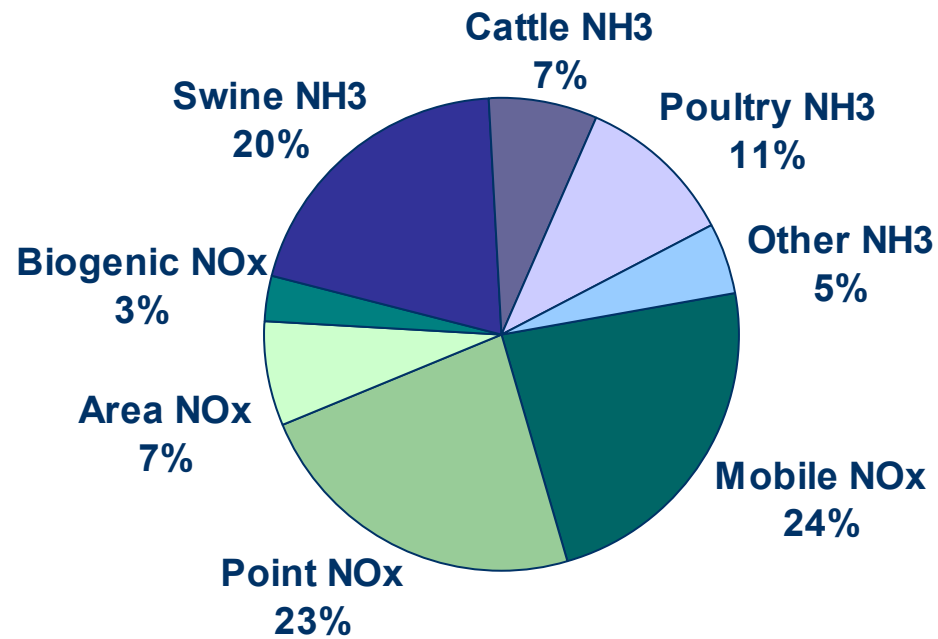


Figure 1.4 North Carolina's Atmospheric Nitrogen Budget. Other ammonia sources include fertilizer application, human waste, and industrial point sources (NCDENR, 1999).

Sources of Atmospheric Ammonia in North Carolina

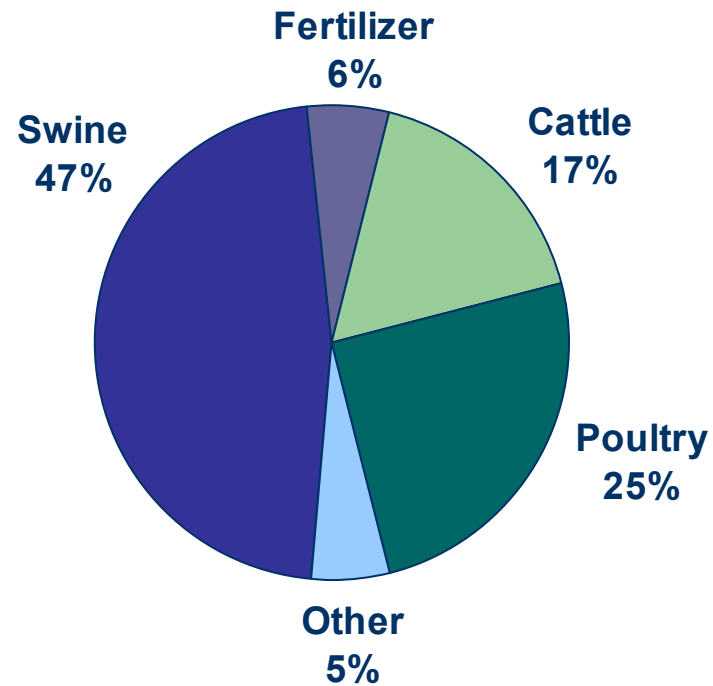


Figure 1.5 North Carolina's Atmospheric Ammonia Budget. Other sources include human waste and industrial point sources (NCDENR, 1999).

Dynamic Flow-Through Chamber System

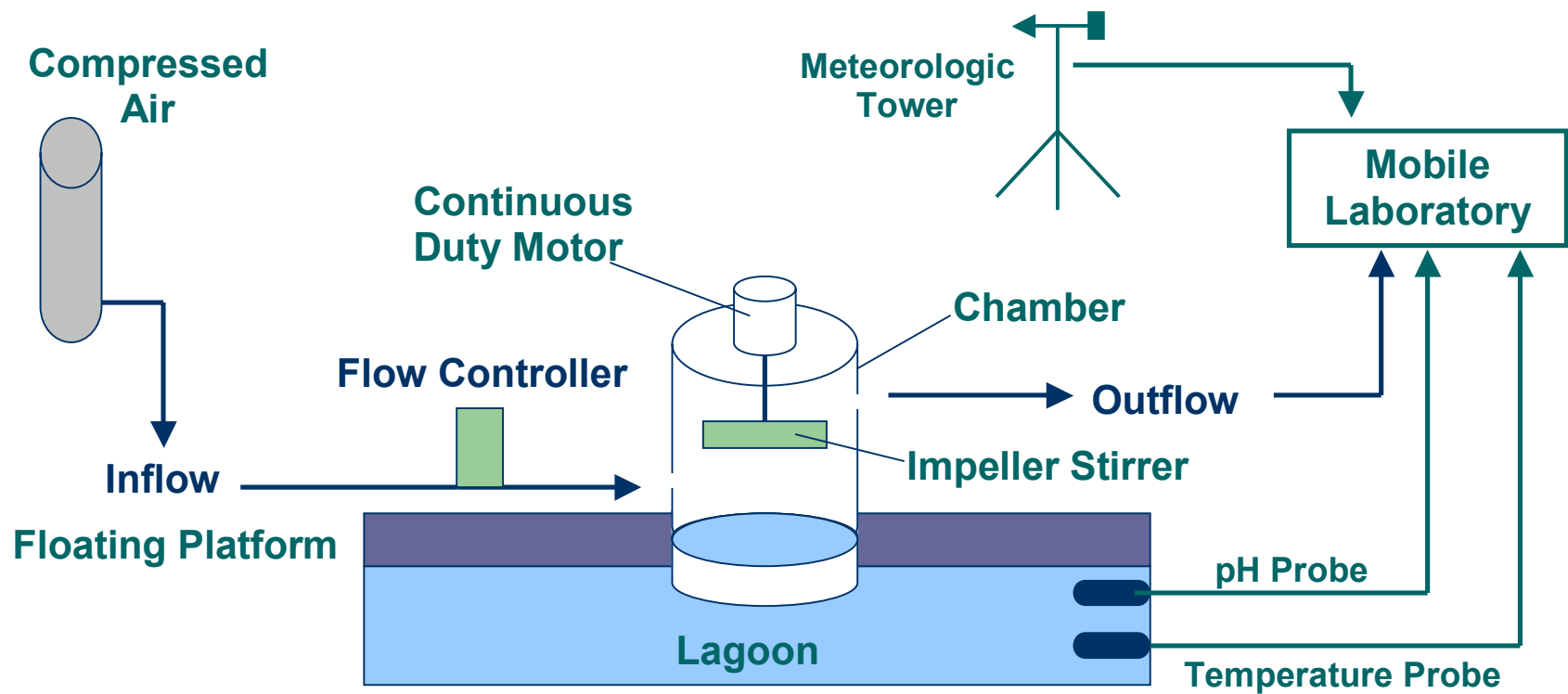


Figure 1.6 Schematic of Dynamic Chamber System and Typical Field Measurement Site Configuration.

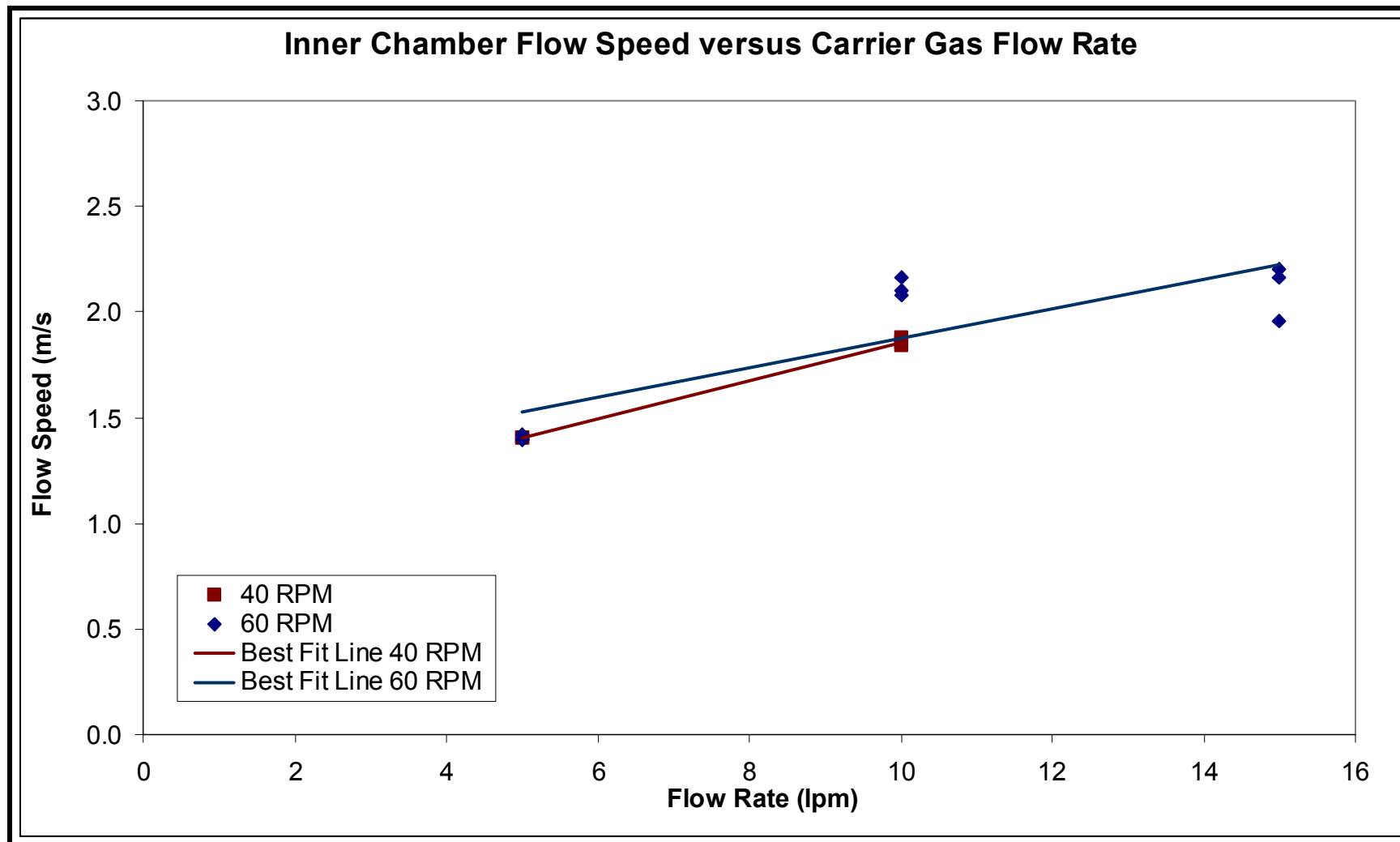
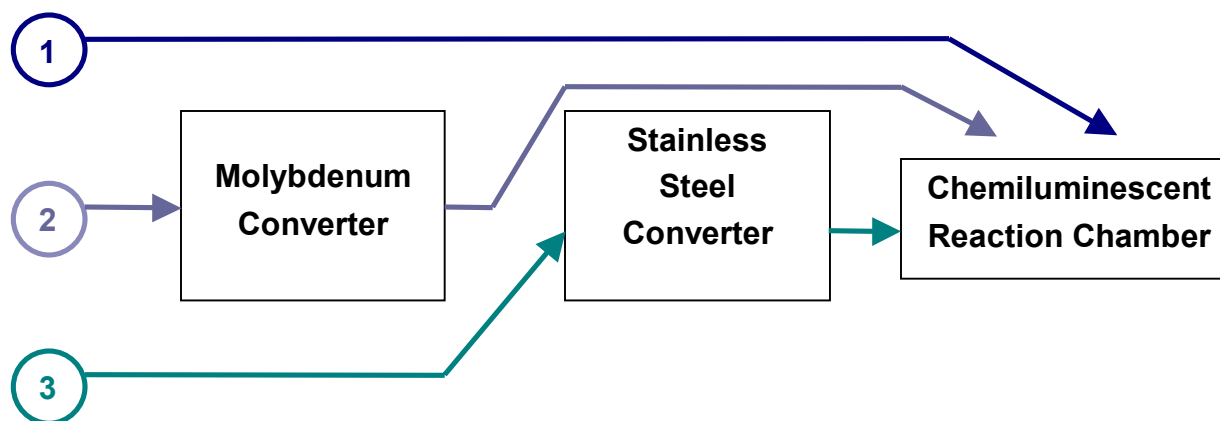


Figure 1.7 Chamber Wind Speed and Carrier Gas Flow Rate. Flow speed indicates the wind speed inside the chamber, referred to as chamber wind speed.

Schematic of Model 17c Ammonia Analyzer



Flow Path	Molybdenum Converter	Stainless Steel Converter	Instrument Reading
1	Bypassed	Bypassed	NO
2	Flow-Through	Bypassed	NO _y
3	Bypassed	Flow-Through	N _T
$[NH_3] = [N_T] - [NO_y]$			

Figure 1.8 Schematic of Thermo Environmental Instruments Model 17c Ammonia Analyzer (TECO, 1999).

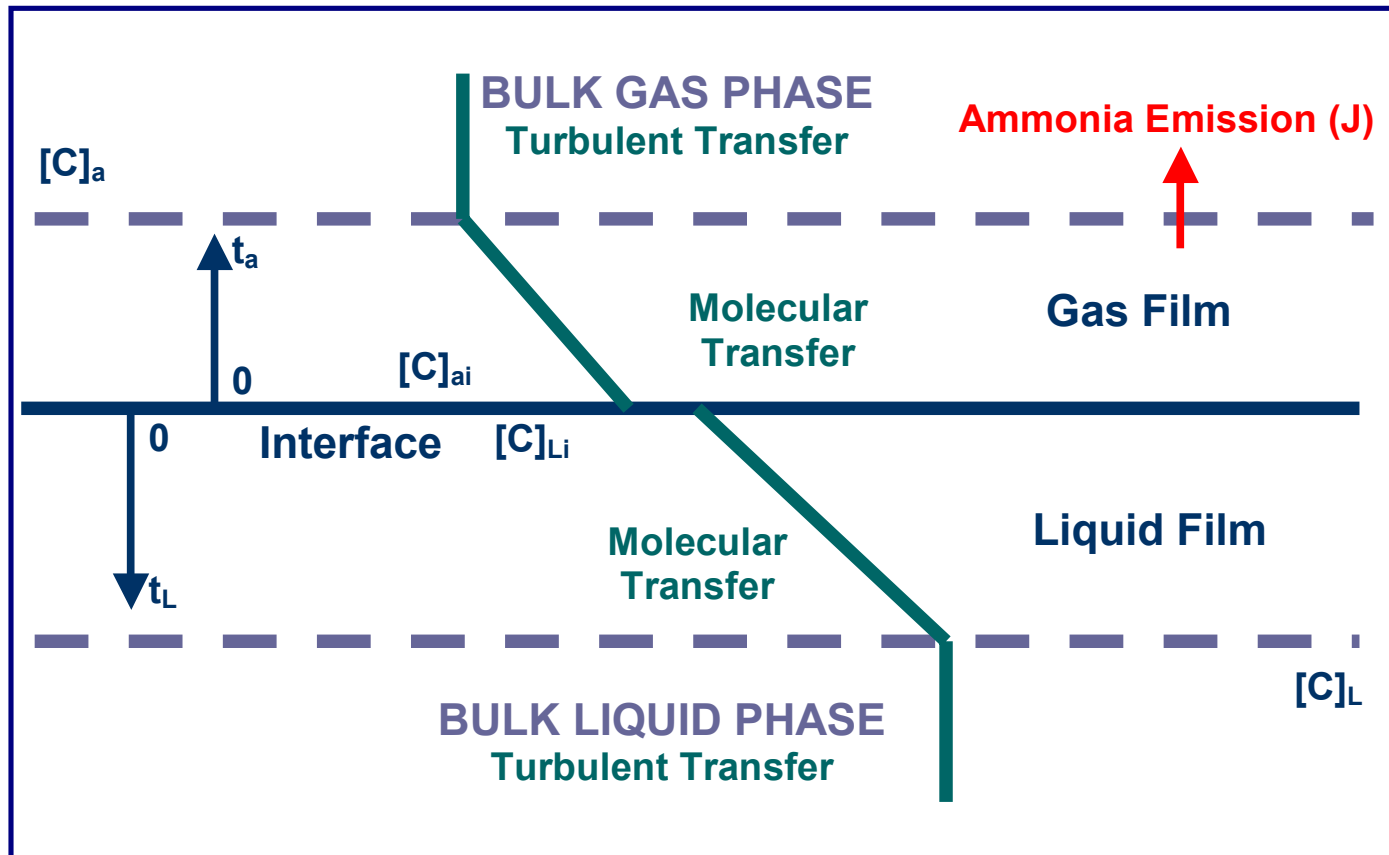


Figure 1.9 Two-Film Theory of Mass Transfer. This theory underlies the coupled mass transfer with chemical reactions model (Aneja et al., 2001b).

CHAPTER II. CHARACTERIZATION OF AMMONIA EMISSIONS FROM ALTERNATIVE SWINE WASTE TREATMENT TECHNOLOGIES

Abstract

Measurements of ammonia flux are conducted from components of experimental swine waste treatment technologies located in eastern North Carolina as part of the Odor, Pathogens, and Emissions of Nitrogen (OPEN) Program. An average flux of 1,433 $\mu\text{gN-NH}_3/\text{m}^2/\text{min}$ is emitted during the April 2002 field campaign from the liquid waste components of Barham Farm's covered anaerobic lagoon system, and an average flux of 805 $\mu\text{gN-NH}_3/\text{m}^2/\text{min}$ is emitted during the June 2002 field campaign from the liquid waste components of Howard Farm's constructed wetland system. An average of 0.3 $\text{gN-NH}_3/\text{min}$ exit the vent of the hog housing unit at Grinnels Laboratory, which has a conveyor belt waste removal system. Ammonia emission factors are estimated from ammonia flux measurements from the liquid waste components at Barham Farm (4.14 $\text{kgN-NH}_3/\text{animal}/\text{yr}$) and Howard Farm (4.56 $\text{kgN-NH}_3/\text{animal}/\text{yr}$). These are only valid for the limited periods of the measurement field campaigns. A multivariate relationship between the natural logarithm of ammonia flux and effluent temperature, pH and Total Ammoniacal Nitrogen (TAN) concentration at each farm elucidates statistically significant effects of the parameters on ammonia flux from Barham and Howard Farm's liquid waste components. The observational model is as follows, $\text{Ln}(\text{N-NH}_3) = -1.925 + 0.092T_L + 0.793\text{pH} + 0.002[\text{TAN}] - 12.650F - 0.006T_L * F + 1.556\text{pH} * F + 0.006[\text{TAN}] * F$, in which F represents farm, with Barham Farm equaling zero and Howard Farm equaling one.

Introduction

Over the past few centuries, anthropogenic activities have perturbed the natural balance of ammonia (NH_3) and other nitrogen compounds. Currently, the human demand for food production requires the extensive use of nitrogen containing fertilizers, as well as the production of domestic livestock on a grand scale. Ammonia volatilizes from the fertilizers and domestic animal waste associated with food production. Estimates of the global ammonia budget indicate that domestic animal waste emits approximately 20 to 35 Tg of ammonia to the atmosphere per year, representing approximately half of the annual global ammonia emissions (Warneck, 2000).

As the dominant gaseous base specie in the atmosphere, ammonia readily combines with and neutralizes acidic compounds, including sulfuric acid, nitric acid and hydrochloric acid, creating ammonium (NH_4^+) aerosols (Hewitt and Davison, 1998; Meszaros, 1993; Finlayson-Pitts, 1986). Ultimately, atmospheric ammonia and ammonium undergo wet or dry deposition to the earth's surface (Warneck, 2000), potentially altering the chemical composition and nutrient balance of soil surfaces, river basins and aquatic ecosystems (Walker et al., 2000; Paerl, 1995).

Ammonia readily combines with moisture in the atmosphere, altering the composition and pH of precipitation (Warneck, 2000), cloudwater (Kim and Aneja, 1992) and atmospheric aerosols (Lefer et al., 1999). Ammonia emissions from extensive commercial swine operations potentially provide a large portion of the atmospheric nitrogen compounds that deposit and contribute to nitrogen loading in North Carolina's sensitive aquatic ecosystems (Paerl, 1997). Excessive nutrient loading in aquatic

ecosystems creates a detrimental condition of accelerated primary productivity or eutrophication.

Ammonia emissions from agricultural operations in the North Carolina have recently attracted much attention due to the rapid expansion of the state's commercial swine industry. The state's hog population has increased from approximately three million to ten million over the past decade (Figure 1.2). Much of the growth of North Carolina's swine industry has occurred in the eastern North Carolina, with the majority of operations concentrated in the Coastal Plain Region (Figure 2.1). Current estimates indicate that atmospheric ammonia emitted from North Carolina's swine facilities accounts for 20% of the state's atmospheric nitrogen budget and 47% of the state's atmospheric ammonia budget (Table 2.1).

Ammonia volatilizes from four principal sources at traditional swine facilities, namely hog production houses (Childers et al., 2001), waste storage and treatment lagoons (Aneja et al., 2001a; Aneja et al., 2000), land application of lagoon slurry to adjacent cropland (Sommer, 1997), and subsequent reemission of ammonia from the soil (Roelle and Aneja, 2001). This study presents ammonia flux measurements made from components of the experimental waste treatment and storage technologies at three swine facilities located in central and eastern North Carolina, namely Barham Farm, Grinnels Laboratory, and Howard Farm. Barham Farm's experimental waste management system incorporates a covered in-ground anaerobic digester along with an original traditional primary waste lagoon that now acts as a storage and overflow pond. Howard Farm's experimental waste management system incorporates a solid separator and constructed wetland cells that process waste. Grinnels Laboratory serves as the first portion of an

experimental belt and gasification waste management system. The laboratory includes a hog housing unit with a conveyor belt system that separates waste for processing at a gasification plant.

The field measurement campaigns included in this study are part of the Odor, Pathogens, and Emissions of Nitrogen (OPEN) Program run by North Carolina State University's Animal and Waste Poultry Management Center. Program OPEN involves 18 swine operations in eastern North Carolina, each of which utilizes an experimental waste treatment technology that is potentially environmentally superior in comparison with traditional waste treatment technologies. Program OPEN scientists quantitatively investigate each farm in order to determine whether its waste treatment technology emits relatively lower concentrations of odor, pathogens, ammonia and other nitrogen compounds in comparison to the traditional lagoon and spray technology.

Specifically, in this study, ammonia flux measurements have been made from the experimental waste treatment lagoon systems at Barham Farm and Howard Farm, from cropland soils at Howard Farm, from the cover of the in-ground anaerobic waste digester at Barham Farm, and from the conveyor belt system located within a hog housing unit at Grinnells Laboratory. Ammonia flux measurements made from the liquid waste components of the alternative waste treatment systems at Barham Farm and Howard Farm include measurements from the storage and overflow ponds at Barham Farm and measurements from constructed wetland cells and a finishing pond at Howard Farm. Barham Farm's original primary waste treatment lagoon has been sectioned off with heavy polymer baffles since the covered in-ground anaerobic waste digester has been constructed. The sections of the original primary waste treatment lagoon are now

referred to as the storage and overflow ponds. Since the construction of the wetland cells at Howard Farm, the original primary waste treatment lagoon has served as a holding pond, referred to as the finishing pond, for waste water before it is applied to adjacent cropland for fertilization.

The ammonia flux measurements from the waste ponds and constructed wetland cells at Barham Farm and Howard Farm are evaluated with respect to ammonia flux measurements made from traditional waste treatment lagoons. The ammonia emissions from the liquid waste components of Barham and Howard Farm's waste management systems are also parameterized with respect to corresponding environmental parameters, including effluent temperature, pH, and Total Ammoniacal Nitrogen concentration, in order to develop a multivariate relationship that elucidates the relative importance of each parameter to ammonia emission. Total Ammoniacal Nitrogen (TAN) concentration represents the total concentration of ammonia and ammonium in the liquid waste.

In summary, the objectives of this study are as follows.

- 1) Quantify ammonia flux from components of Barham and Howard Farms' experimental waste management systems and from the hog housing unit of Grinnels Laboratory's experimental waste management system as part of Program OPEN.
- 2) Evaluate ammonia flux from the waste ponds and wetland cells at Barham and Howard Farms with respect to ammonia flux from traditional hog waste treatment lagoons in order to evaluate the effectiveness of the liquid waste components of the experimental waste management systems.

- 3) Estimate ammonia emission factors for ammonia emissions from the liquid waste components of Barham and Howard Farms in order to investigate the implications of measured ammonia emissions from these components of the experimental waste management systems.
- 4) Characterize ammonia flux from the liquid waste components with respect to corresponding environmental parameters, including effluent temperature, pH, and TAN concentration, in order to ascertain the relative influence of each parameter on ammonia flux via a multivariate analysis.

Methods and Materials

Sampling Sites

In-Ground Ambient Temperature Anaerobic Digester System

Sampling occurred at Barham Farms in Clayton, North Carolina during the first two weeks of April 2002. The alternative waste treatment technology at this farm consists of a covered anaerobic waste lagoon system (Figure 2.2). An impermeable layer of high density polypropylene covers the new primary anaerobic waste treatment lagoon in order to prevent gaseous methane and other pollutants from entering the atmosphere during the digestion process. The methane gas is extracted and burned in a biogas generator that powers a water heater used for the farm's production activities. The effluent from the digester flows into a second stage lagoon, referred to as the storage pond, which is a sectioned portion of the original primary waste lagoon. The waste then flows into biofiltration devices that use bacteria to oxidize the reduced forms of nitrogen in the effluent to nitrate. The biofiltered waste is stored in a smaller portion of the overflow pond, sectioned off by heavy polymer baffles. The biofiltered water replenishes

water in the hog houses and flows to two greenhouses adjacent to the hog production facilities, where the nitrate in the water fertilizes plant and vegetable species. The overflow pond adjoins with the storage pond, with a heavy polymer baffle separating the two, and is also a sectioned portion of the original primary waste treatment lagoon. Rainwater and effluent that occasionally spills over from the storage pond fill the overflow pond, along with water that flows out of the greenhouses.

This farrow-to-wean operation includes sows, gilts, boars, and piglets up to three weeks old. Four gestation and two farrowing barns accommodate approximately 4,000 pigs at any given time, each of which obtains 5 to 10 lbs of feed per day and weighs an average of 450 to 500 lbs. This study includes ammonia flux measurements made from the surface of the storage pond, the overflow pond and the polypropylene cover of the waste lagoon. The ammonia emissions from Barham Farm have dimensions of mass per area per time, as they derive from area sources.

Belt Manure Removal and Gasification System

For one week at the end of April 2002, ammonia emissions were measured from an alternative waste treatment technology located within Grinnels Laboratory in the Department of Animal Science at North Carolina State University in Raleigh. This operation constitutes the first half of the belt and gasification process included in Program OPEN. At Grinnels Laboratory, a conveyor belt system located within the experimental hog housing unit separates solid and liquid waste (Figure 2.3). The hog housing unit within the laboratory measures 20 ft by 60 ft and contains five pens. This grower-finishing operation includes gilts and boars weighing from 50 to 150 lbs. During periods of steady state activity, the unit houses approximately 80 pigs, and each pig

ingests 3.5 lbs of feed per day. This study includes ammonia emission measurements made directly outside the housing unit's ventilation system. These emissions have units of mass per time, as Grinnels Laboratory acts as a point source.

Constructed Wetland System

For two weeks at the beginning of June 2002, ammonia flux was measured from a waste treatment system designed in the form of a wetland ecosystem at Howard Farms located in Richlands, North Carolina. At this farm, a constructed wetland cell system treats the wastewater effluent after a solid separator divides the waste into solid and liquid components (Figure 2.4). The wetlands cell system consists of an inner wetland cell, an outer wetland cell, and the finishing pond, which is the original primary waste lagoon. The solid waste is applied to crops as fertilizer. The plant species and microbes contained within the wetland cells break down the liquid effluent. Once processed by the wetland cells, the effluent enters the finish water holding pond where it remains until used for land application. Howard Farm is a finishing operation that consists of four hog houses and 3,520 pigs weighing an average of 135 lbs each. This study includes ammonia flux measurements made from the inlet, midpoint and outlet of the wetland cells, from the finishing pond, and from the soil of adjacent cropland. Ammonia emissions from Howard Farm have dimensions of mass per area per time, as they derive from area sources.

Ammonia Flux Measurement

A dynamic flow-through chamber system with continuous impeller stirring (Figure 1.6) (Aneja et al., 2000; Chauhan, 1999; Aneja et al., 1996; Kim et al., 1994; Kaplan et al., 1988) is used to measure ammonia flux from liquid waste and soil surfaces,

such as the surfaces of the waste ponds and constructed wetland cells at Barham and Howard Farms and the cropland soil surfaces at Howard Farm. For measurements over liquid waste surfaces, the system consists of a four foot by four foot floating plywood platform and a plastic cylindrical chamber. The translucent chamber fits into a circular hole cut in the center of the platform and penetrates the liquid surface by approximately 8 cm. The seal formed between the bottom of the cylinder and the lagoon water ensures a closed system inside the chamber. Fluorinated ethylene propylene (FEP) Teflon lines the entire inner surface of the chamber. The chamber has a diameter of 25.4 cm, an internal height of 45.72 cm, and a volume of 23,167 cm³. A carrier gas of compressed air flows through the system at variable rates, with flow rates ranging from 4.45 to 10.80 lpm in this study. A mass flow controller adjusts and records the flow rates. A variable speed Teflon impeller stirrer, set between 40 rpm and 60 rpm in this study, keeps the air within the chamber ideally mixed. The entire closed system consists of Teflon tubing, Teflon lining or stainless steel fittings in order to minimize chemical reactions with the sample stream. A vent on the sample line exiting the chamber prevents the system from over pressurizing. The vent is periodically bubble tested during sampling periods to check for under pressurization or leaks in the system.

After approximately 30 minutes of running the carrier gas through the chamber and sample lines, any accumulated ammonia within the chamber has been flushed out and the chamber has reached steady state (Aneja et al., 2000). At this point, the sample line is connected to a Thermo Environmental Instruments (TECO) Model 17c chemiluminescence ammonia analyzer in order to quantify the concentration of ammonia within the sample stream exiting the chamber. The sample stream entering the ammonia

analyzer separates into three parts. In the first flow path, the sample mixes with ozone, and all of the nitric oxide within the sample reacts to produce a reading of nitric oxide concentration via the standard chemiluminescence technique. In the second flow path, the sample passes through a molybdenum converter (325°C) which converts all oxidized forms of nitrogen to nitric oxide. The converted sample then reacts with ozone in order to quantify the concentration of all nitrogen oxides (NO_y). In the third flow path, a stainless steel converter (750°C) converts all nitrogen oxides and ammonia into nitric oxide, which results in a reading of total nitrogen (N_T). The concentration of ammonia equals the difference between the signal for total nitrogen and the signal for nitrogen oxides (TECO, 1999). Ammonia concentration readings from the ammonia analyzers are stored in a Campbell Scientific Instruments 21x micrologger at 15 minute intervals. The micrologger receives a signal from the ammonia analyzers every second and stores these signals in a temporary format. The micrologger averages the temporary data every 15 minutes and permanently stores the averaged values. The ammonia analyzers are located in a mobile laboratory contained within a modified Ford Aerostar van. The van has a 13,500 BTU air conditioning unit that regulates the climate for effective performance of the ammonia analyzers.

For ammonia flux measurements from soils, the chamber is placed in a stainless steel ring, which is inserted into the soil a few hours prior to the start of the flux measurements. O-rings around the rim of the chamber create a seal, ensuring a closed system. A Campbell Scientific temperature probe monitors the soil temperature during soil flux measurement periods. The stainless steel ring and the chamber were fastened to the polypropylene cover at Barham Farm in order to measure any ammonia emission due

to diffusion through the lagoon cover. Air temperature inside the chamber was also monitored while measuring ammonia flux from the cover.

In order to quantify ammonia flux from a hog house, such as the alternative waste treatment technology located within a hog housing unit at Grinnels Laboratory, the ammonia concentration exiting the house vent is measured. Lines of Teflon tubing draw air exiting the vent into the ammonia analyzers located within the mobile laboratory. A 42 mm, 1 μ m pore size Teflon filter prevents particles from entering the system. The filter is mounted in a one stage filter pack attached to the sample line inlet. Ammonia emissions from the housing unit are estimated by multiplying the ammonia concentration exiting the vent by the flow rate through the vent.

Sampling Scheme

Before beginning a daily or diurnal sampling period, the carrier gas flows through the chamber system for approximately 30 minutes before the sample is introduced to the ammonia analyzers in order to flush accumulated ammonia from the chamber and to allow the system to reach steady state (Aneja et al., 2000). Between each daily or diurnal sampling period, the floating chamber system is moved to another location on the liquid within a 10 m radius of the mobile laboratory, for the sample and sensor lines that run between the floating platform and the mobile laboratory stretch approximately 10 m. Due to the location constraints, stratified random sampling is performed. In order to capture the various subsections of each farm's waste treatment system, the mobile laboratory, meteorological tower, and floating chamber system must be periodically moved. The ammonia analyzers are calibrated before sampling begins at each new subsection. Each field campaign lasts for approximately two weeks.

Calibration of the ammonia analyzers is performed using certified standard mixtures of nitric oxide and ammonia, zero grade air, and a Thermo Environmental Instruments 146 dilution/titration instrument. Nitric oxide is used to calibrate the oxidized nitrogen and total nitrogen channels, and ammonia is used to calibrate the ammonia channel. A multipoint calibration of the ammonia analyzers is conducted prior to each measurement campaign. Zero and span checks occur approximately every other day during the campaign, and the multipoint calibration is rechecked at the conclusion of each measurement period.

Ammonia Flux Calculation

The following mass balance expression (Equation 2.1) describes the chemical and physical dynamics within the flow-through chamber system used to quantify ammonia flux for this study.

$$\frac{dC}{dt} = \left[\frac{qC_o}{V} + \frac{JA}{V} \right] - \left[\frac{LA_w}{V} + \frac{LA}{V} + \frac{q}{V} \right] (C) - R \quad (2.1)$$

In this equation, J equals the ammonia flux across the liquid waste surface. A, V, and A_w represent the chamber's cross sectional area, volume, and surface area of the inner chamber walls above the liquid surface. Compressed air flows through the chamber at rate q. L and R denote the loss of ammonia by reaction with the chamber walls and by reaction within the gaseous state, respectively. C_o is the ammonia concentration entering the chamber, and C equals the ammonia concentration at all points within the chamber and at the chamber outlet. The ammonia concentration within the chamber is uniform and equals that exiting the chamber because this type of system performs as a Continuously Stirred Tank Reactor (CSTR), which implies that all elemental units of air within the chamber have the same composition (Aneja, 1976).

Using compressed air as a carrier gas, the initial concentration of ammonia at the inlet of the chamber is negligible. Due to a short residence time of the sample stream within the chamber system and the use of compressed air as a carrier gas, the gaseous ammonia emitted across the liquid surface does not chemically react to a significant extent, so R is also negligible. As the system approaches equilibrium, the instantaneous change in ammonia concentration with time approaches zero. Therefore, at steady state dC/dt equals zero. These conditions give rise to the following reduced form of the mass balance equation at steady state (Equation 2.2).

$$J = \left[(L) \left(\frac{2}{r} + \frac{1}{h} \right) + \frac{q}{V} \right] (C)(h) \quad (2.2)$$

r and h denote the radius and height of the chamber, respectively. The flow rate, chamber dimensions and steady state ammonia concentration are measured, while the loss term is determined experimentally. Based on the method of Kaplan et al. (1988), the

loss term depends on the slope of the plot of $-\ln \left[\frac{C_{eq} - C(t)}{C_{eq} - C_o} \right]$ versus time (t). For this

experiment, C_o equals the ammonia concentration measured from the chamber system after it reaches an initial equilibrium state with a constant carrier gas flow rate. C_{eq} equals the concentration of ammonia measured from the chamber system once it has reached a second equilibrium state at a reduced carrier gas flow rate. $C(t)$ represents the concentration of ammonia at any time, t , during the transition between the two equilibrium states. L is a function of the dimensions of the chamber and the slope of the best fit line through the points of the plot. The loss term calculated for this study equals 0.01723 m/min and represents the average result from four loss term experiments performed at different times throughout the field measurement periods.

Environmental Parameters

Two Campbell Scientific temperature probes simultaneously measure the effluent temperature, one located within the chamber and one placed 50 cm from the chamber. An Innovative Sensors pH probe placed 50 cm from the chamber continuously monitors the effluent pH during ammonia flux measurement periods. Daily waste water samples taken adjacent to the floating platform are submitted to a laboratory in the Biological and Agricultural Engineering Department at North Carolina State University for analysis of TAN. The waste water analysis occurs in the Weaver Laboratory via colorimetric analysis with a sodium based color reagent. The pH of the waste water samples is also measured in the laboratory analysis. A meteorological tower containing air temperature, relative humidity, solar radiation, wind speed and wind direction sensors continuously monitor the ambient conditions.

Results and Discussion

Table 2.2 summarizes the mean ammonia flux and associated parameters measured at each farm. The amount of ammonia that diffuses through the lagoon cover to the atmosphere at Barham Farm closely resembles the amount of ammonia emitted from the cropland soils at Howard Farm. Ammonia emissions from both the soils and the cover are much lower in magnitude than ammonia emissions from the liquid surfaces per square meter, yet substantial ammonia emissions may derive from the soil and cover surfaces, depending on the total surface area of their influence.

The cropland soils at Howard Farm had not recently been fertilized with waste during the ammonia flux measurement period. Roelle (2001) reports that soils fertilized with wastewater slurry emitted an average of thirty-two times more ammonia than

unfertilized soils. In the future, measurements of ammonia flux from recently fertilized soils should take place, as well as further exploration into the possibility of ammonia emission from the covered lagoon at Barham Farm. Such investigations would help to illuminate the effects of all segments of the waste treatment systems of Program OPEN farms. Along with the liquid waste surfaces and cropland soils of commercial hog operations, hog houses also emit significant amounts of ammonia to the atmosphere. Program OPEN incorporates measurements of ammonia emissions from these point sources as well.

Emission Factors

Ammonia emission factors for the liquid waste portions of the waste management technologies at Barham and Howard Farms may be estimated by assuming that the average ammonia fluxes measured from the waste storage ponds and wetland cells remain constant across the liquid surfaces. The surface areas of the storage pond and the overflow pond at Barham Farm equal approximately 4,500 m² and 19,400 m², respectively. With an average measured ammonia flux of 1,545 µgN-NH₃/m²/min from the storage pond and 1,271 µgN-NH₃/m²/min from the overflow pond, the waste ponds at Barham Farm emit an estimated total of 32 gN-NH₃/min. During the field campaign, Barham Farm had approximately 4,000 hogs. During this two week period, representative of the spring season, Barham Farm's waste ponds emitted an estimated 4.14 kgN-NH₃ per animal per year.

Similarly, the various subsections of Howard Farm's liquid waste system emitted an estimated 31 gN-NH₃/min, with the wetlands cells and finishing pond measuring approximately 29,600 m² and 7,400 m², respectively, and with average measured

ammonia fluxes of $927 \mu\text{gN-NH}_3/\text{m}^2/\text{min}$ and $419 \mu\text{gN-NH}_3/\text{m}^2/\text{min}$ from the wetland cells and the finishing pond, respectively. During the measurement period in June 2002, Howard Farm housed approximately 3,520 animals. During this period, representative of the summer season, Howard Farm's wetland cells and finishing pond emitted an estimated 4.56 kgN-NH_3 per animal per year.

The emission factor estimated for the liquid waste surfaces at Barham Farm relies on ammonia flux data measured in the spring season, while the emission factor estimated for the wetland cells and finishing pond at Howard Farm incorporates ammonia flux data measured in the summer season, even though the emission factors are expressed as per year. However, due to variations in environmental parameters and operational procedures, the average ammonia flux may have seasonal variations. Thus, estimated ammonia emission factors can also vary seasonally throughout the year.

The ammonia emissions measured outside the vent at Grinnels Laboratory average $0.3 \text{ gN-NH}_3/\text{min}$. Grinnels Laboratory houses approximately 80 animals and therefore emits an estimated 1.96 kgN-NH_3 per animal per year. The ammonia emissions from Grinnels Laboratory may not vary according to seasonal changes, for the system is contained within a controlled laboratory environment, yet the measured ammonia emissions may vary in response to perturbations in the laboratory operations. The Project Investigator for Grinnels Laboratory, Dr. Theo van Kempen, has determined that the laboratory operations were not optimal during the April 2002 measurement campaign, for the swine living at the facility during that time period had been suffering from an illness. Thus, additional measurements of ammonia flux made from Grinnels Laboratory under optimal conditions must be considered in the future. Note also that the belt system at

Grinnels Laboratory represents only the first part of a belt and gasification system.

Ammonia emissions from the second half of the system should also be considered in the future in order to constrain the ammonia emissions deriving from the entire system.

Table 2.3 summarizes the emission factors estimated from the wetland cells and waste ponds at Barham Farm and Howard Farm, from the hog housing unit of Grinnels Laboratory's belt system, and from other swine operations in previous studies. An estimated 0.4 kgN-NH₃, 1.1 kgN-NH₃, 2.2 kgN-NH₃, and 5.2 kgN-NH₃ are emitted per animal per year from a traditional primary waste lagoon at a farm in Sampson County, North Carolina, during the winter, fall, spring and summer seasons, respectively.

In a study of a swine farm located in eastern North Carolina, McCulloch et al. (1998) report that waste lagoons, animal houses, and surrounding crops emit an estimated range of 4.88 kgN-NH₃ per animal per year to 9.52 kgN-NH₃ per animal per year. The estimated range of ammonia emission factors is based on data taken in the summer season. A study performed in the United Kingdom by Dragosits et al. (1998) reports that waste lagoons, animal houses, and surrounding crops emit an estimated 3.18 kgN-NH₃ per animal per year. Battye et al. (1994) report an estimated 7.58 kgN-NH₃ per animal per year are emitted by waste lagoons, animal houses, and surrounding crops. A modeling study of ammonia transport in Europe by Asman and van Jaarsveld (1992) reports that waste lagoons, animal houses, and surrounding crops emit an estimated 4.41 kgN-NH₃ per animal per year.

Overall, the ammonia emission factors calculated from Barham and Howard Farm's waste ponds and wetland cells and from Grinnels Laboratory fall within the range of ammonia emission factors calculated from traditional waste lagoons, animal houses,

and surrounding cropland of agricultural operations in North Carolina and abroad. In the future, ammonia emissions from the other components of Barham and Howard Farms, such as hog houses, can be incorporated into the emission factor analysis in order to obtain an emission factor for each experimental system overall. Such emission factors would be more comparable to the reported emission factors that incorporate waste lagoons, animal houses, and surrounding crops. Differences in emission factors arise due to the use of different waste treatment technologies, differences in animal management and feed practices, meteorological and seasonal variation, and experimental error.

Traditional and Experimental Waste Management

On average, ammonia fluxes measured from a traditional waste treatment lagoon at a farm located in Sampson County, North Carolina, exceed the ammonia fluxes measured from the liquid waste components of Barham Farm's and Howard Farm's waste management systems. Data measured from the traditional lagoon exhibits a distinct seasonal pattern with average ammonia fluxes varying from 4,017 $\mu\text{gN-NH}_3/\text{m}^2/\text{min}$ to 1,706 $\mu\text{gN-NH}_3/\text{m}^2/\text{min}$ to 844 $\mu\text{gN-NH}_3/\text{m}^2/\text{min}$ to 305 $\mu\text{gN-NH}_3/\text{m}^2/\text{min}$ in the summer, spring, fall, and winter seasons, respectively. Ammonia fluxes measured from the traditional lagoon in the spring and summer seasons exceed those measured from Barham Farm in the spring and from Howard Farm in the summer. In the future, ammonia flux measurements made at Barham Farm and Howard Farm during different seasons can be analyzed along with the present data in order to potentially decipher seasonal patterns at the experimental operations. Table 2.4 summarizes the average ammonia flux measurements and corresponding environmental

parameters from the liquid waste components of Barham Farm and Howard Farm and from the traditional waste lagoon.

Ammonia Flux and Temperature

Lagoon temperature measurements made from Barham Farm range from 6 °C to 24 °C, and Howard Farm's lagoon temperatures range from 20 °C to 31 °C. Ammonia flux and lagoon temperature measurements from Barham Farm and Howard Farm exhibit similar diurnal trends with daily maximum values occurring in the afternoon, as illustrated in Figure 2.5 and Figure 2.6. Each point in the figures represents 15 minute averaged ammonia flux or lagoon temperature.

A negative correlation exists between ammonia flux and effluent temperature from both farms, for the ammonia flux from Barham Farm's liquid waste components exceed those from Howard Farm's liquid waste components, while effluent temperatures measured in June at Howard Farm exceed those measured in April at Barham Farm. However, for the individual datasets from Barham Farm and Howard Farm, effluent temperature is positively correlated with ammonia flux. A correlation analysis of 15 minute averaged ammonia flux measurements and corresponding effluent temperature data from each farm separately demonstrates positive correlations between ammonia flux and effluent temperature at Barham Farm ($r=0.75999$) and at Howard Farm ($r=0.49491$). Note that the correlation analysis does not take the variables into account simultaneously.

The ammonia flux data measured at Grinnels Laboratory also exhibits a positive correlation with the room temperature within the laboratory. The diurnal trend of ammonia flux is illustrated in Figure 2.7, and the relationship between room temperature and ammonia flux is demonstrated in Figure 2.8.

A combination of physical and chemical processes can dictate the influence of temperature on ammonia flux from waste treatment lagoons. For example, in a traditional waste treatment lagoon, the rate of decomposition of waste sludge at the bottom of a lagoon increases with lagoon temperature, which in turn increases the amount of ammonia within the lagoon. As the ammonia volatilizes from the lagoon to the atmosphere, more ammonia deriving from decomposition at the bottom of the lagoon diffuses upward and replenishes the ammonia in the upper layers of the lagoon. An increase in temperatures increases the rate of transfer of ammonia across the liquid-gas interface (Ibusuki and Aneja, 1984), expediting this cycle. Because the waste lagoons are not physically mixed, diffusion and mass transfer processes primarily distribute the ammonia within a traditional waste treatment lagoon (Muck and Steenhuis, 1982).

Ammonia Flux and TAN

Measurements of TAN concentration from Barham Farm range from 358.0 to 559.0 mgN/l, while measurements of TAN concentration from Howard Farm range from 29.6 to 306.0 mgN/l. A positive correlation ($r=0.56973$) exists between ammonia flux measurements and effluent TAN concentration at Barham and Howard Farms, with the TAN concentration and ammonia flux from Barham Farm's storage and overflow ponds exceeding those from Howard Farm's wetland cells and finishing pond (Figure 2.9). The correlation analysis incorporates 15 minute averaged ammonia flux measurements and corresponding effluent TAN data, and the simple linear regression (Figure 2.9) incorporates daily averaged ammonia flux measurements and corresponding effluent TAN data. The large distinction in TAN concentration seemingly underlies the

difference in ammonia flux measured from the effluent of the two farms, yet other parameters such as effluent temperature and pH must be taken into account as well.

TAN denotes the amount of ammonia and ammonium contained within the effluent. TAN derives in part from the break down of organic nitrogen, a temperature dependent process. Total Kjeldahl Nitrogen (TKN) equals TAN plus organic nitrogen and oxidized nitrogen in the effluent. Since anaerobic conditions prevail in traditional hog waste treatment lagoons, TKN consists of primarily TAN and organic nitrogen in such environments. The amount of TKN and TAN in a traditional waste lagoon depends on such factors as animal population, animal weight, and animal feeding patterns. In a traditional waste treatment lagoon operating at steady state conditions, the amount of organic nitrogen within the waste lagoon does not vary to a significant extent. A balance exists between the inflow and outflow of nitrogen from traditional waste treatment lagoons. In the liquid waste portions of the experimental technologies, additional biological, chemical and physical processes confound the cycling of nitrogen throughout the systems. Thus, it is important to simultaneously consider the influence of multiple variables on ammonia flux from the liquid waste portions of Barham and Howard Farms' waste management systems.

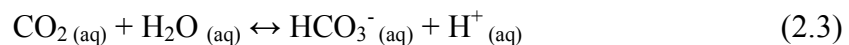
Ammonia Flux and pH

The effluent pH measured adjacent to the dynamic chamber system ranges from 7.14 to 8.47 at Barham Farm and from 6.84 to 8.29 at Howard Farm. Each day, waste water samples are taken adjacent to the floating chamber and are analyzed for water chemistry. The effluent pH measured from the lagoon water samples range from 7.88 to 8.20 at Barham Farm and from 7.23 to 8.11 at Howard Farm. On average, the pH

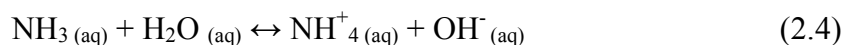
measured from the waste water samples exceeds the continuously monitored pH by 0.15 ± 0.42 . A positive correlation ($r=0.33929$) exists between ammonia flux measurements and the corresponding effluent pH measured from waste water samples at Barham and Howard Farms (Figure 2.10). The correlation analysis incorporates 15 minute averaged ammonia flux measurements and corresponding effluent pH data, and the simple linear regression model (Figure 2.10) incorporates daily averaged ammonia flux measurements and corresponding effluent pH data. Modeling studies (Aneja et al., 2001b; Sommer et al., 1991) also discern a positive correlation between lagoon pH and ammonia flux.

The difference between the two types of pH measurements could arise due to differences in sampling times, contaminated lagoon water samples, a malfunction by the pH sensor, or a change in lagoon water chemistry over time. The discrepancy should be investigated in order to decipher which type of measurement more accurately reflects the state of the waste lagoon. For instance, in order to check for a change in pH of the lagoon samples over time, the pH of the lagoon samples could be measured by the continuous sensor just before the samples are submitted to the laboratory for analysis.

Waste lagoon slurry has a high buffer capacity that confines lagoon pH to a relatively narrow range, as observed in this and other studies (Aneja et al., 2001a; Aneja et al., 2000; Bunton, 1999). The bicarbonate ion, a product of the hydrolysis of urea and microbial conversion of organic matter, maintains lagoon pH in waste treatment lagoons and neutralizes hydrogen ions released into solution by ammonium, as illustrated in Equation 2.3 (Sommer et al, 1991).



The pH of the wastewater slurry dictates the equilibrium point between ammonia and ammonium in solution. Ammonia and ammonium exist in aqueous equilibrium according to Equation 2.4 (Warneck, 2000).



As the pH of the lagoon increases, the concentration of OH^- increases, causing the equilibrium to shift to the left. As the equilibrium shifts left, the proportion of ammonia in the solution increases, creating more ammonia that can volatilize to the atmosphere. Conversely, if the water content of a lagoon increases, the equilibrium shifts to the right, increasing the amount of ammonium in solution. The pH of the wastewater slurry varies as the conditions within the lagoon change. Initially, the wastewater has more inorganic carbon than ammonia and ammonium (Olesen and Sommer, 1993). Carbon dioxide volatilizes from the lagoon surface more quickly than ammonia, due to the higher solubility of ammonia. As the carbon dioxide levels decrease, the pH of the lagoons increases. An increase in lagoon pH increases the amount of ammonia available for volatilization. Ammonia then escapes into the atmosphere. Ultimately, as ammonia continues to escape to the atmosphere, the lagoon pH begins to decrease (Bunton, 1999).

Multivariate Analysis

Multiple variables simultaneously affect ammonia flux from traditional waste treatment lagoon surfaces and from experimental liquid waste treatment surfaces. In order to more clearly discern the effects of multiple environmental parameters on ammonia flux from the waste ponds and wetland cells at Barham Farm and Howard Farm, a multivariate analysis incorporating effluent temperature, pH, and TAN has been performed. A multiple regression highlights the effects of the parameters on ammonia

flux from the liquid waste components of two distinct waste management systems across two different seasons. The multiple regression includes 15 minute averaged ammonia flux and effluent temperature measurements and corresponding effluent pH and TAN data from the waste ponds and wetland cells at Barham and Howard Farms. The model incorporates farm as a variable in order to account for differences in responses to lagoon temperature, pH, and TAN between farms. For the purposes of the multivariate model, Barham Farm equals zero, and Howard Farm equals one. The multivariate analysis also accounts for autocorrelation, for the data points are in 15 minute intervals.

The multiple regression reveals statistically significant relationships between ammonia flux and effluent temperature ($t=6.37$, $p<0.0001$), ammonia flux and pH ($t=2.11$, $p<0.0352$), and ammonia flux and TAN ($t=5.66$, $p<0.0001$), with a significance level of 95%. Furthermore, the overall response surface for ammonia flux differs between farms ($t=-4.14$, $p<0.0001$), as indicated by the farm variable. The response of ammonia flux to pH ($t=4.04$, $p<0.0001$) and TAN ($t=12.44$, $p<0.0001$) also differs between farms, as indicated by the interaction terms. The observational model is as follows (Equation 2.5)

$$\begin{aligned} \text{Ln (N-NH}_3\text{)} = & -1.925 + 0.092T_L + 0.793\text{pH} + 0.002[\text{TAN}] - \\ & 12.650F - 0.006T_L * F + 1.556\text{pH} * F + 0.006[\text{TAN}] * F \end{aligned} \quad (2.5)$$

The statistics associated with the multiple regression analysis are summarized in Table 2.5. Lagoon temperature, pH and TAN have positive and significant effects on ammonia flux from each farm.

The increase in ammonia flux with effluent temperature become apparent when considering effluent temperature simultaneously with effluent TAN or effluent pH. The overall increase in ammonia flux with effluent temperature and TAN is illustrated in

Figure 2.11, while Figure 2.12 illustrates increases in ammonia flux with effluent temperature and pH. Each point in the figures represents a 15 minute averaged ammonia flux and effluent temperature measurement and corresponding effluent pH or TAN data resulting from the laboratory analysis of the waste water samples. The positive correlation between ammonia flux and effluent temperature for the overall dataset also becomes evident in the multiple regression model, shown above. Thus, a multivariate analysis supports the conclusion that an increase in effluent temperature leads to an increase in ammonia flux, when taking into account the differences in water chemistry between farms.

Conclusions

The ammonia emissions discussed in this study serve as evaluation criteria for the sustainable efficiency of three experimental hog waste treatment technologies located in eastern North Carolina as part of Program OPEN. An estimated 45 kgN-NH₃ are emitted per day from Barham Farm's overflow and storage ponds, while an estimated 44 kgN-NH₃ are emitted per day from Howard Farm's overflow and storage ponds. The hog housing unit at Grinnels Laboratory emits an estimated 0.4 kgN-NH₃ per day. Larger amounts of ammonia per square meter are emitted from the liquid components of Barham Farm's ($1,433 \pm 484 \mu\text{gN-NH}_3/\text{m}^2/\text{min}$) and Howard Farm's ($805 \pm 589 \mu\text{gN-NH}_3/\text{m}^2/\text{min}$) waste management systems than from the cropland soil at Howard Farm ($17 \pm 10 \mu\text{gN-NH}_3/\text{m}^2/\text{min}$) or from the polypropylene cover at Barham Farm ($19 \pm 2 \mu\text{gN-NH}_3/\text{m}^2/\text{min}$). However, the ammonia emissions from the soil or cover surfaces may prove to be substantial, depending on the surface area of their influence. Further investigation of ammonia flux from cropland soils and from the polypropylene cover should occur in the

future in order to further elucidate the influence of these sources of atmospheric ammonia.

Grinnels Laboratory has a lower estimated annual emission factor (1.96 kgN-NH₃/animal/yr) than Barham Farm's (4.14 kgN-NH₃/animal/yr) or Howard Farm's (4.56 kgN-NH₃/animal/yr) waste ponds and wetland cells, yet the emission factor for Grinnels Laboratory represents emissions from a hog housing unit, while the emission factors estimated for Barham Farm and Howard Farm represent emissions from liquid waste surfaces. Ammonia emissions from other components of Barham and Howard Farms, such as hog housing units, should be incorporated into the estimated emission factors in order to establish emission factors that represent all of the components of the experimental swine operations. Furthermore, Grinnels Laboratory represents only the first of two stages in a belt and gasification project. Ammonia emissions from the gasification plant also need to be considered in the future. Emission factors calculated from ammonia flux measurements made under different meteorological and operational conditions should also be considered in the future in order to estimate ammonia emissions under a variety of circumstances.

Ammonia fluxes from Barham Farm's waste ponds and Howard Farm's wetland cells and finishing pond are positively correlated with effluent temperature, pH, and TAN. A multivariate analysis reveals that ammonia fluxes from the liquid waste portions of Barham Farm and Howard Farm exhibit statistically significant increases with increases in effluent temperature, pH, and TAN concentration. Further theoretical investigation of the parameters that effect ammonia emissions from liquid waste

components of waste management systems occurs in the next chapter, which involves the modeling of ammonia flux across a gas-liquid interface.

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Table 2.1 North Carolina's Atmospheric Nitrogen Budget (NCDENR, 1999).

Source	Nitrogen Species	Estimated Tons of Nitrogen Emitted per Year	% of Total
Highway Mobile	NO _x	78,509	23.31
Point Sources	NO _x	77,798	23.10
Area & Non-Road Mobile	NO _x	24,452	7.26
Biogenic	NO _x	9,926	2.95
Swine	NH₃	68,540	20.35
Cattle	NH ₃	24,952	7.41
Broilers	NH ₃	13,669	4.06
Turkeys	NH ₃	16,486	4.89
Fertilizer Application	NH ₃	8,270	2.46
"Other" Chickens	NH ₃	6,476	1.92
Industrial Point Sources	NH ₃	1,665	0.49
Human	NH ₃	1,629	0.48
Publicly Owned Treatment Works	NH ₃	4,440	1.32
Total		336,812	100

Table 2.2 Summary of Mean Ammonia Flux and Associated Parameters.

	Subsection	Ammonia Flux	Effluent Temperature*	Effluent pH	Effluent TAN	Air Temperature
		$\mu\text{gN-NH}_3/\text{m}^2/\text{min}$	(°C)		(mgN/l)	(°C)
Barham Farm	Overall	1433±484	17.68±3.66	8.09±0.18	455±191	12.17±6.72
	Storage Pond	1545±577	18.46±2.54	7.97±0.06	514±38	9.37±6.60
	Overflow Pond	1271±221	16.64±4.55	8.26±0.13	367±7	15.85±4.83
	Lagoon Cover	19±2	26.44±3.44	---	---	23.00±1.91
Howard Farm	Overall	805±589	24.87±1.56	7.70±0.25	98±88	22.75±5.08
	Wetland Cells	927±623	24.12±1.65	7.71±0.28	117±90	22.10±5.21
	Finishing Pond	419±142	27.46±1.78	7.67±0.00	35±0	24.96±3.88
	Cropland Soil	17±10	26.91±2.52	---	---	26.12±4.21
Grinnell's Laboratory**	Overall	298±67	---	---	---	30.08±1.19

*Soil temperature and chamber air temperature were monitored when measuring flux from the soils and the cover, respectively.

**Ammonia flux has units of mg/min, and in this case, air temperature implies room temperature inside the laboratory.

Table 2.3 Calculation and Comparison of Ammonia Emission Factors.

Study			Average Calculated Ammonia Flux	Surface Area of Emission	Total Estimated Emission	Animal Population at Steady State	Estimated Emission Factor
			μgN-NH ₃ /m ² /min	m ²	gN-NH ₃ /min	Count	kgN/animal/yr
This Study*	Barham Farm	Storage Pond	1,545	4,459	31.54	4000	4.14
		Overflow Pond	1,271	19,398			
	Howard Farm	Wetland Cells	927	29,591	30.54	3520	4.56
		Finishing Pond	419	7,428			
	Grinnels Laboratory		298,472	---	0.30	80	1.96
Aneja et al., 2000*	Primary Lagoon – Summer		4,017	25,000	100.43	10,000	5.2
	Primary Lagoon – Spring		1,706	25,000	42.65	10,000	2.2
	Primary Lagoon – Winter		305	25,000	7.63	10,000	0.4
	Primary Lagoon – Fall		844	25,000	21.1	10,000	1.1
McCulloch et al., 1998			---	---	---	---	4.88-9.52
Dragosits et al., 1998			---	---	---	---	3.18
Battye et al., 1994			---	---	---	---	7.58
Asman and van Jaarsveld, 1992			---	---	---	---	4.41

*These ammonia emission factor calculations encompass ammonia emissions from liquid effluent alone, with the exception of Grinnels Laboratory, whereas the other studies include ammonia emissions from waste lagoons, animal houses, and surrounding crops.

Table 2.4 Ammonia Fluxes from a Traditional Lagoon and from Barham and Howard Farms' Liquid Waste (Aneja et al., 2000).

Farm	Ammonia Flux $\mu\text{gN-NH}_3/\text{m}^2/\text{min}$	Effluent Temperature (°C)	Effluent pH	Effluent TAN (mgN/l)
Barham Farm Spring	1433±484	17.7±3.7	8.09±0.18	455±191
Howard Farm Summer	805±589	24.9±1.6	7.70±0.25	98±88
Sampson County Annual Average	2766±1568	25.6±7.2	7.77±0.06	543±16
Sampson County Summer	4017±987	30.0±3.3	7.50±0.18	551±24
Sampson County Spring	1706±552	24.7±3.2	7.70±0.06	513±41
Sampson County Fall	844±401	11.6±2.2	8.00±0.06	564±29
Sampson County Winter	305±154	12.1±2.1	7.80±0.13	545±33

Table 2.5 Statistical Summary of Multivariate Analysis of Ammonia Flux Measurements from Barham and Howard Farms.

Multivariate Model	Parameter Estimate	Standard Error	t- value	p-value
Intercept	-1.9252	2.9801	-0.65	0.5184
Effluent Temperature (T _L)	0.0922	0.0145	6.37	<0.0001
Effluent pH (pH)	0.7930	0.3760	2.11	0.0352
Effluent TAN ([TAN])	0.0024	0.0004	5.66	<0.0001
Farm (F)	-12.6502	3.0578	-4.14	<0.0001
Temperature Interaction (F*T _L)	-0.0064	0.0162	-0.39	0.6954
pH Interaction (F*pH)	1.5562	0.3856	4.04	<0.0001
TAN Interaction (F*[TAN])	0.0059	0.0005	12.44	<0.0001
$\text{Ln}(\text{NH}_3\text{-N Flux}) = -1.925 + 0.092T_L + 0.793\text{pH} + 0.002[\text{TAN}] - 12.650F - 0.006(F*T_L) + 1.556(F*\text{pH}) + 0.006(F*[\text{TAN}])$				

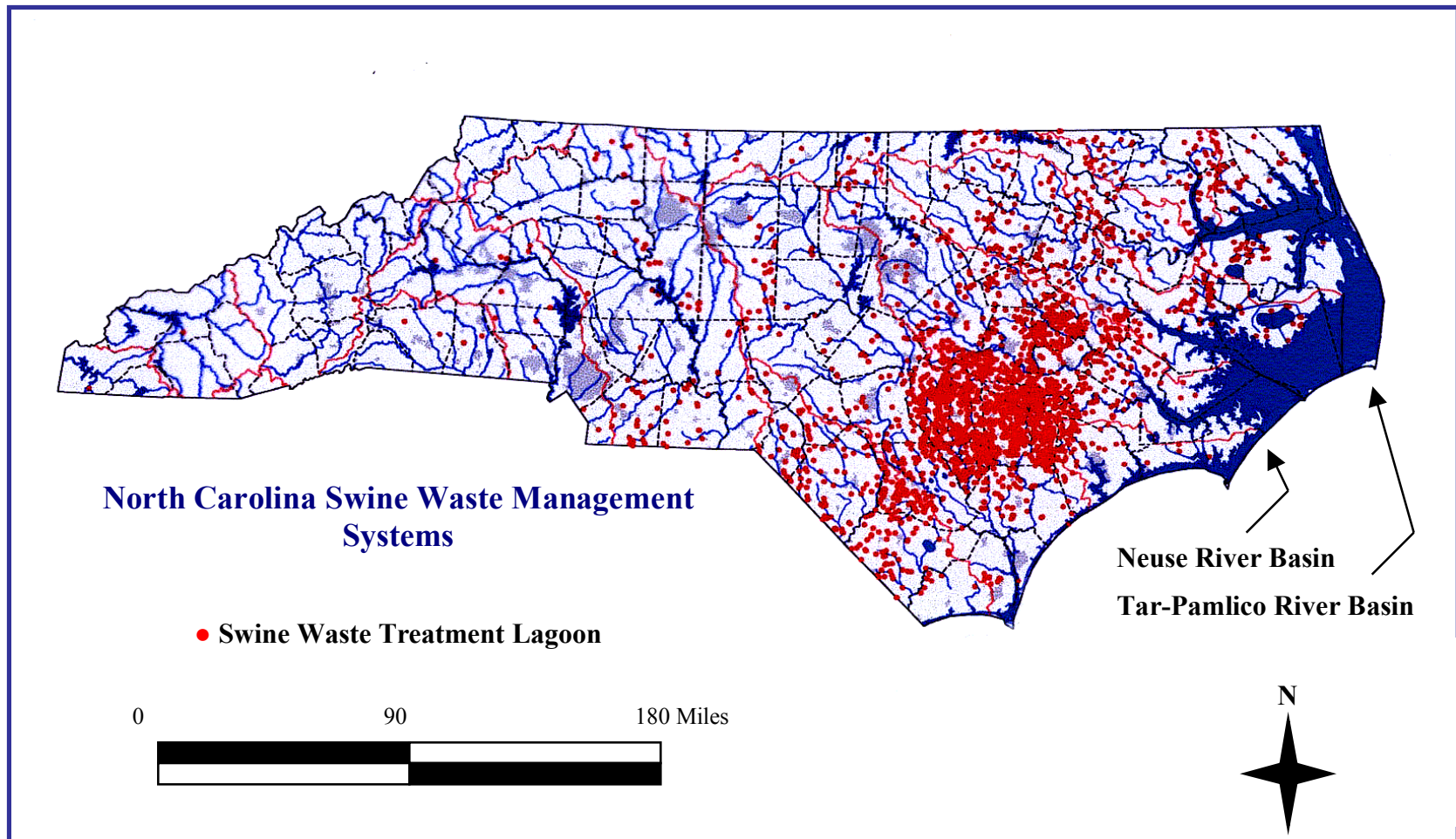


Figure 2.1 Distribution of Swine Waste Treatment Lagoons in North Carolina, according to the North Carolina Department of Natural Resources' registry of confined feedlots.

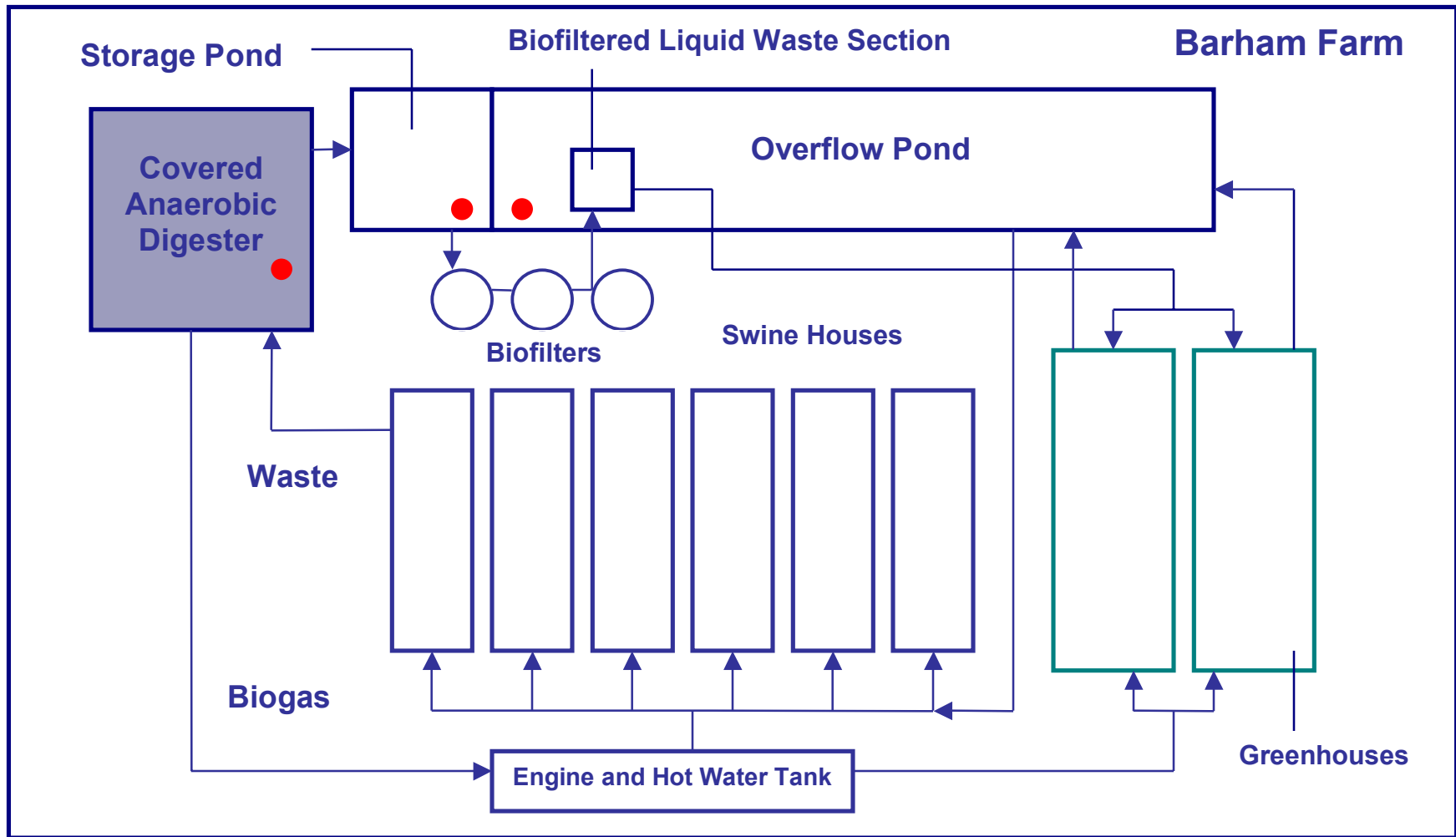


Figure 2.2 Schematic of Barham Farm's Integrated Swine Waste Management System. Not to scale. Ammonia flux measurements were made from the storage pond, the overflow pond, and the lagoon cover, as highlighted.

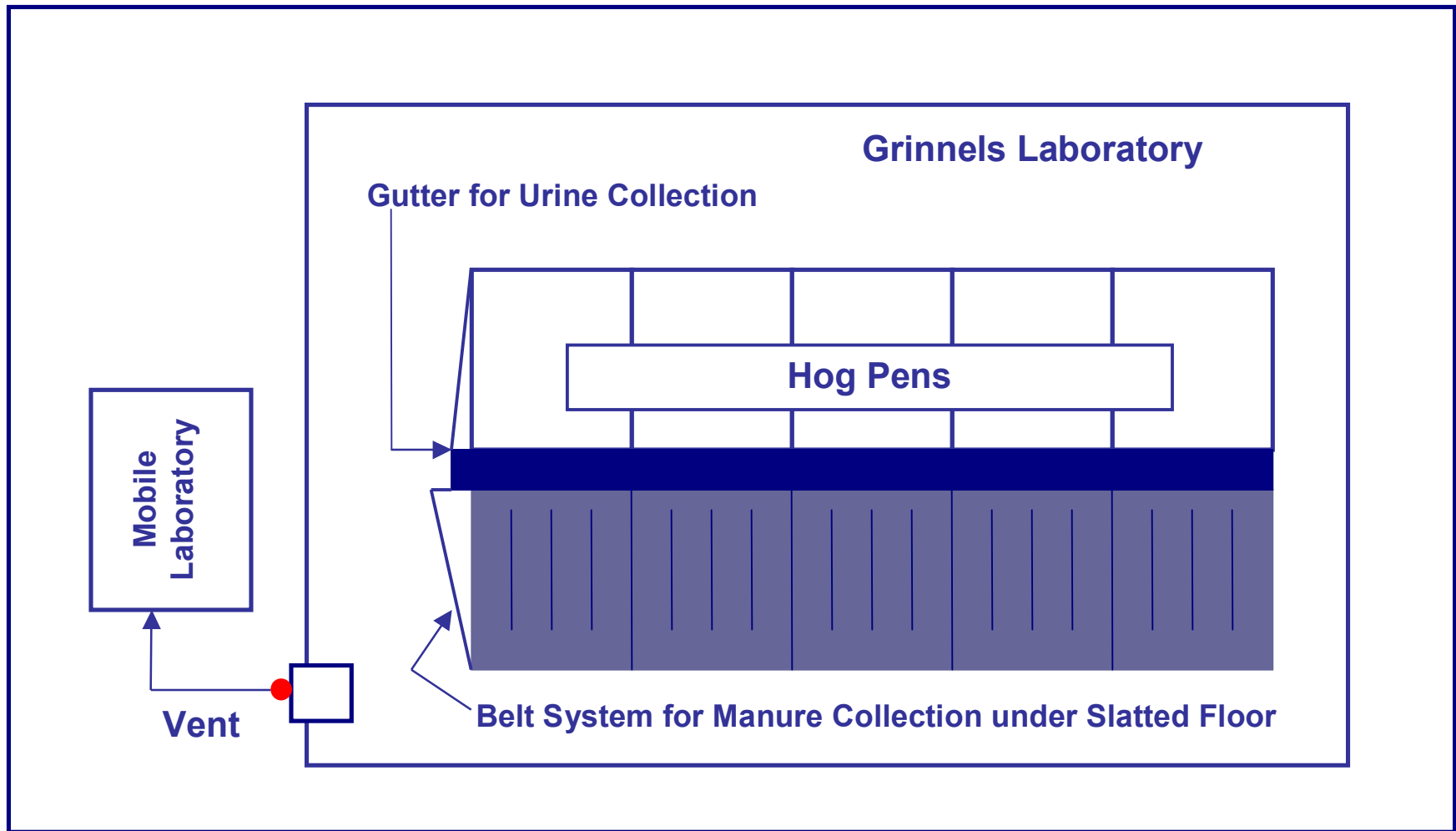


Figure 2.3 Schematic of the In-house Waste Treatment Technology at Grinnels Laboratory. Not to scale. Ammonia measurements were made outside the vent as highlighted.

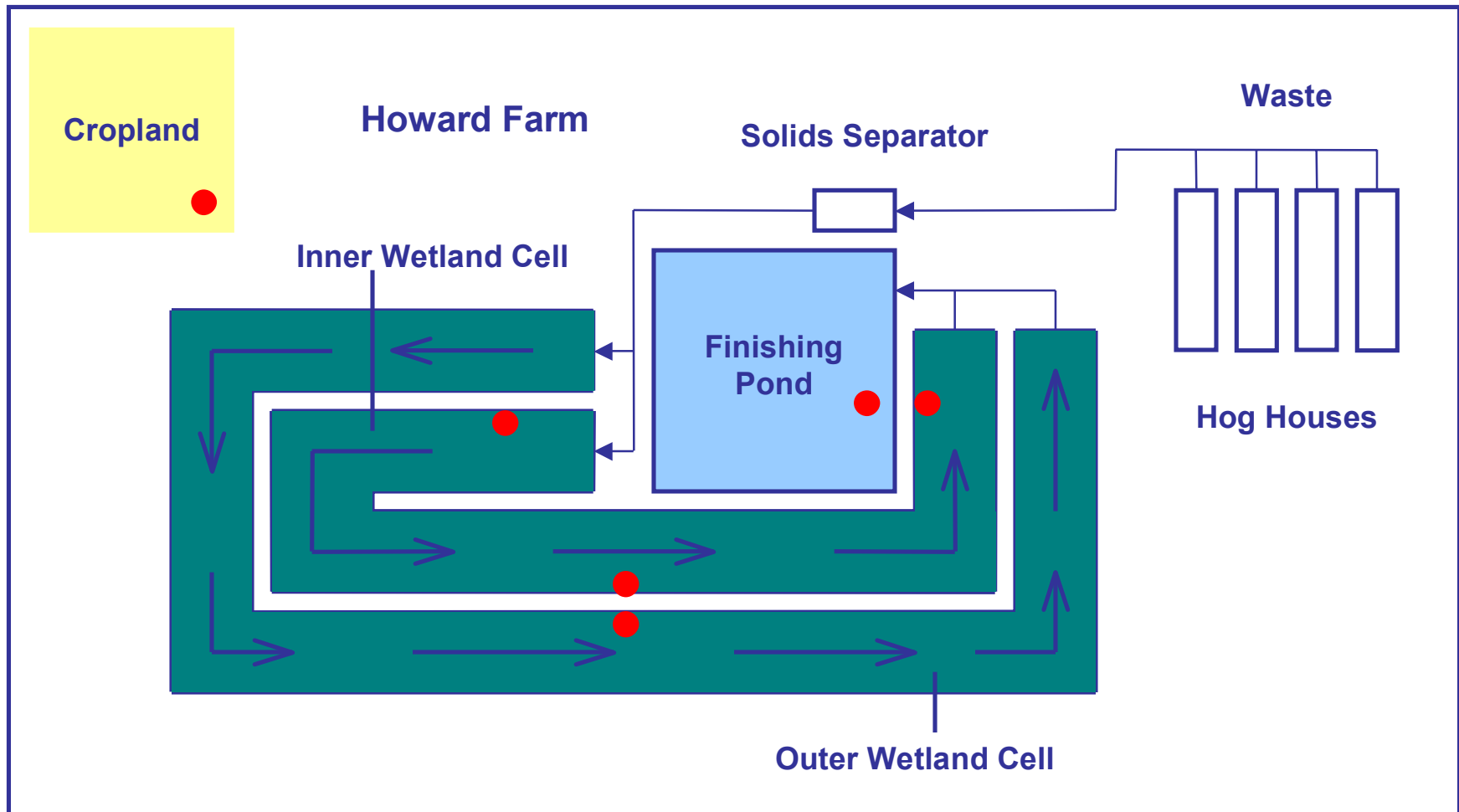


Figure 2.4 Schematic of Howard Farm's Constructed Wetland Swine Waste Management System. Not to scale. Ammonia flux measurements were made at the points highlighted in red.

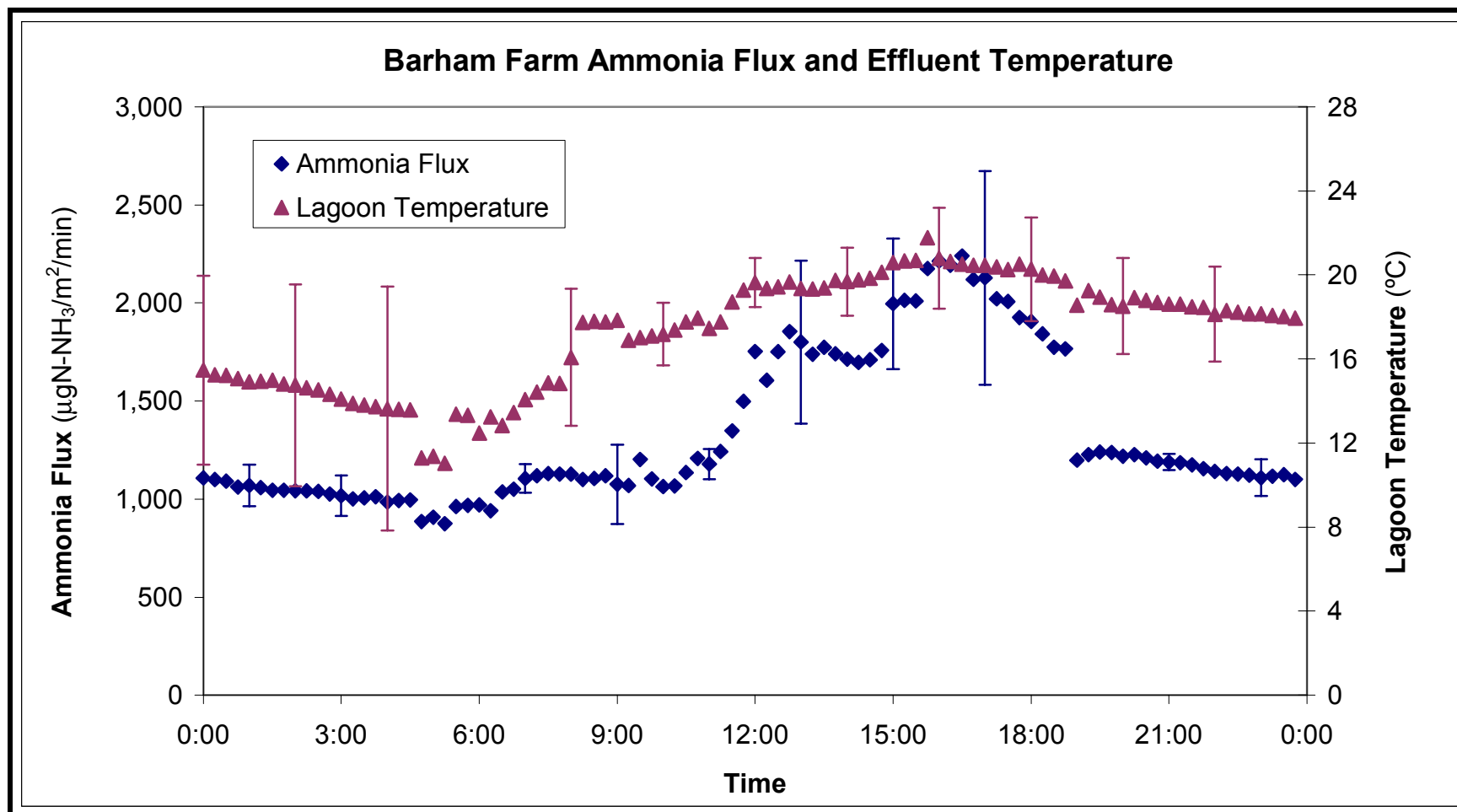


Figure 2.5 Diurnal Pattern of Ammonia Flux and Effluent Temperature at Barham Farm. Each data point consists of a 15 minute averaged ammonia flux ($\mu\text{gN-NH}_3/\text{m}^2/\text{min}$) or effluent temperature ($^{\circ}\text{C}$).

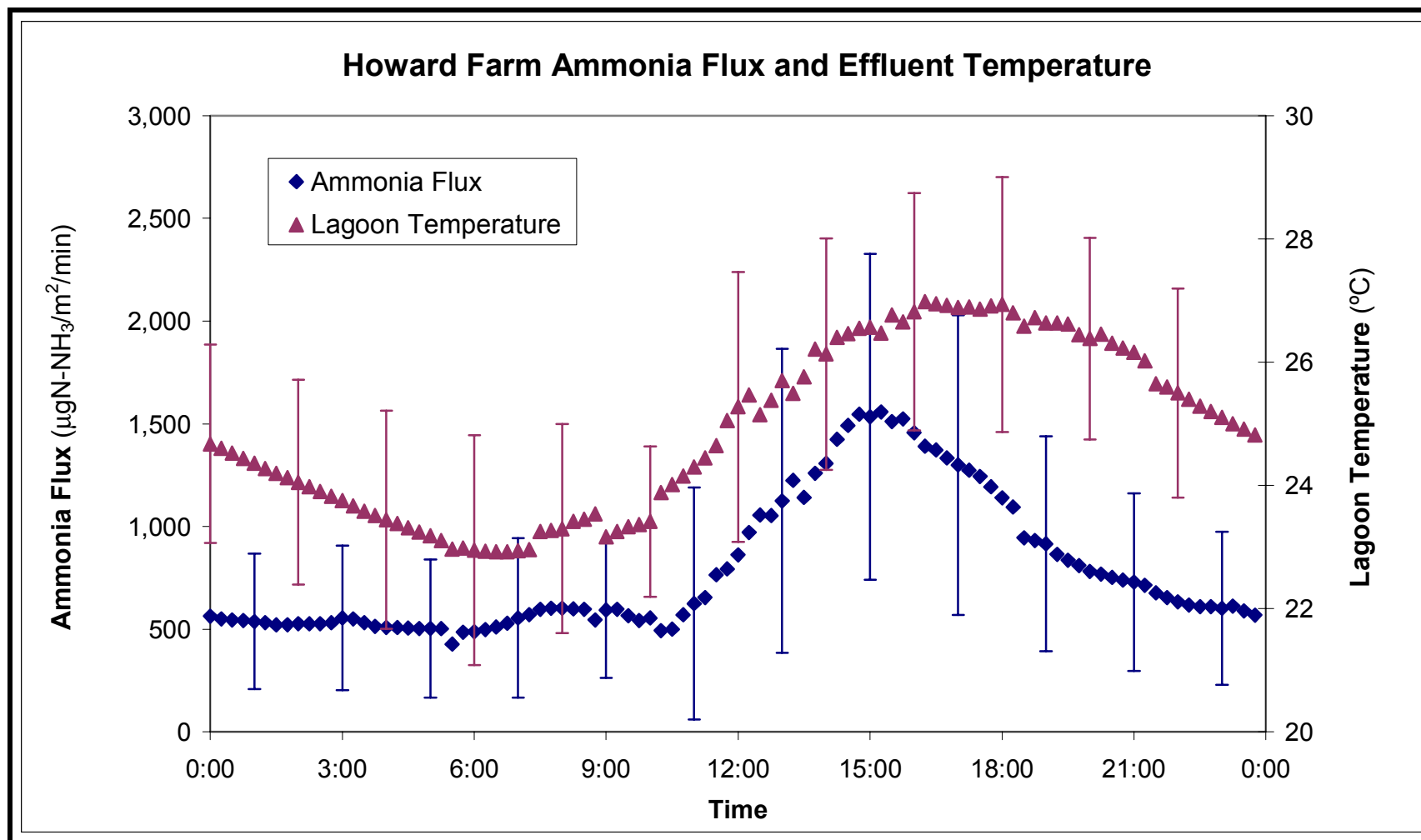


Figure 2.6 Diurnal Pattern of Ammonia Flux and Effluent Temperature at Howard Farm. Each data point consists of a 15 minute averaged ammonia flux ($\mu\text{gN-NH}_3/\text{m}^2/\text{min}$) or effluent temperature ($^{\circ}\text{C}$).

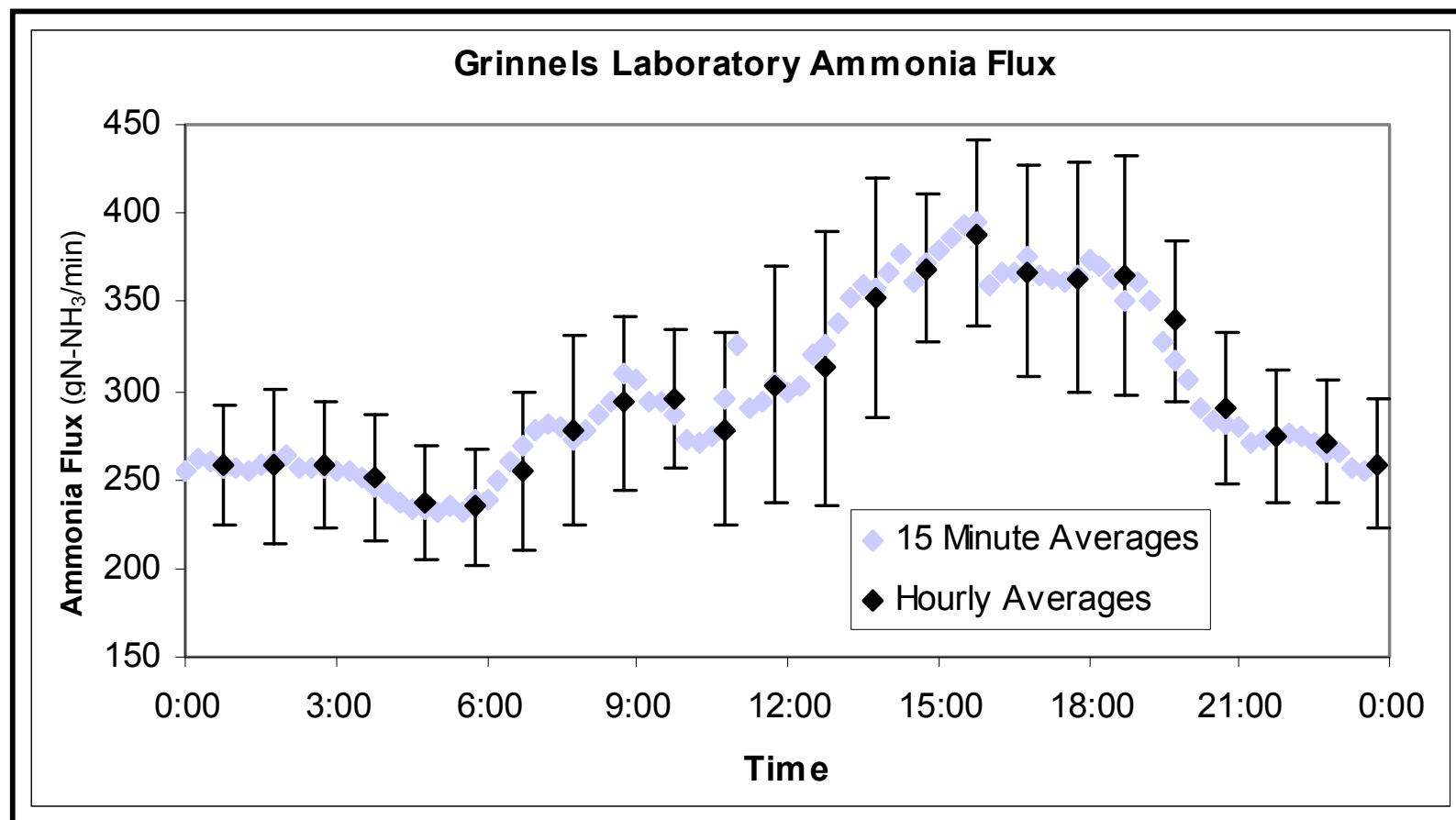


Figure 2.7 Diurnal Pattern of Ammonia Flux from Grinnels Laboratory. Each point consists of a 15 minute or hourly averaged ammonia flux measurement (gN-NH₃/min).

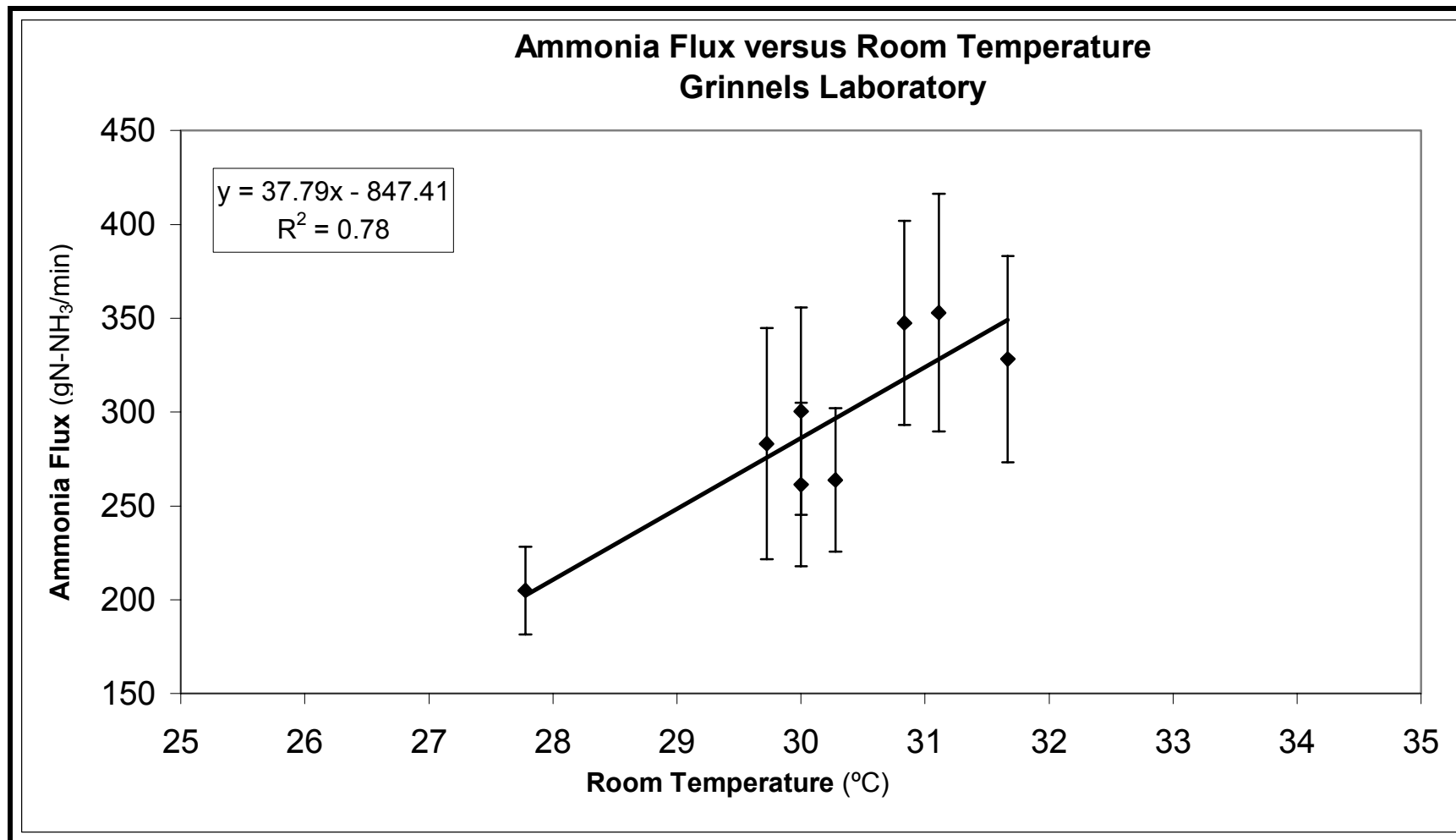


Figure 2.8 Ammonia Flux Versus Room Temperature from Grinnels Laboratory. Each point consists of a daily averaged ammonia flux (gN-NH₃/min) and corresponding room temperature (°C).

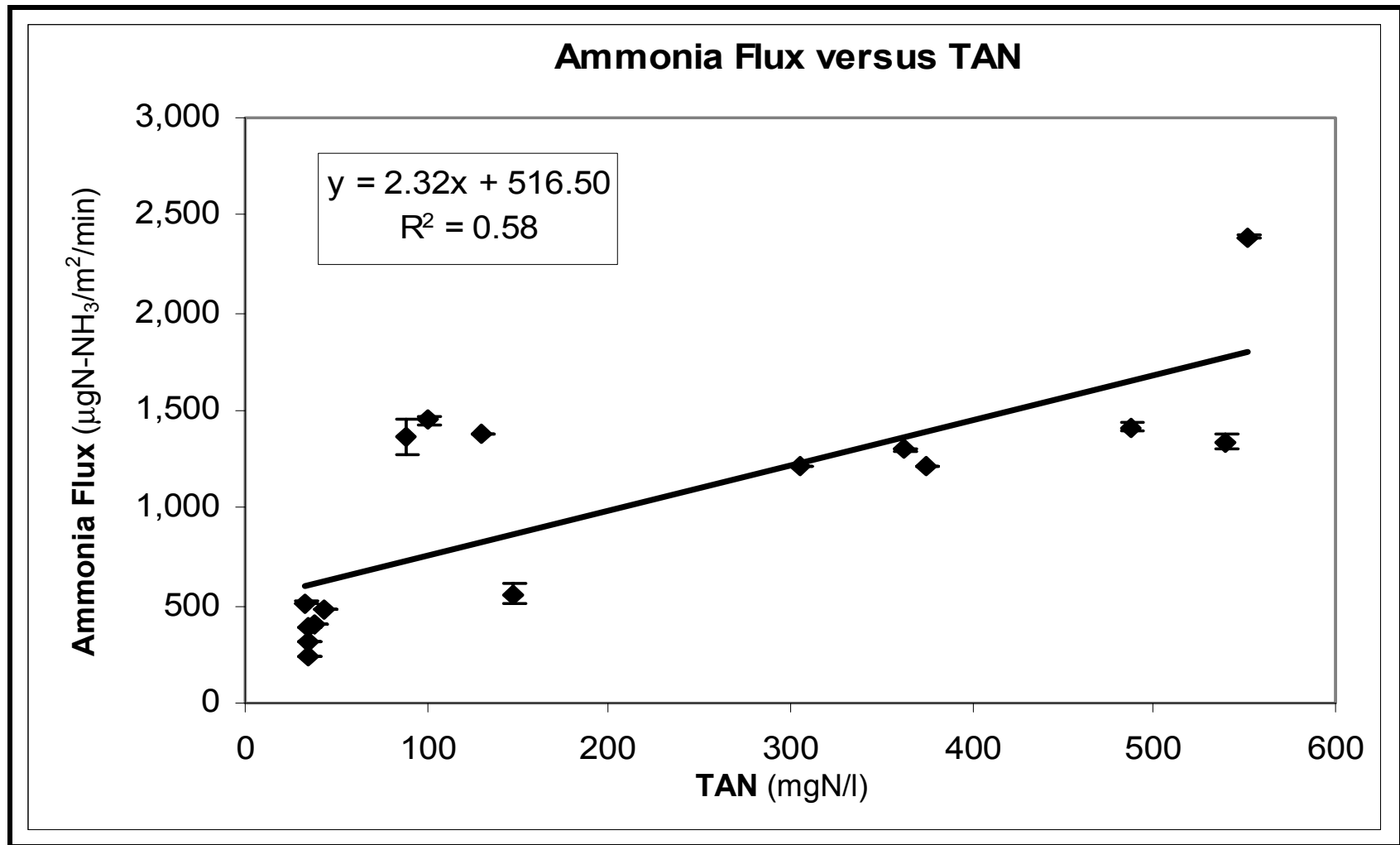


Figure 2.9 Ammonia Flux Versus Effluent TAN Concentration. Each data point consists of a daily averaged calculated ammonia flux ($\mu\text{gN-NH}_3/\text{m}^2/\text{min}$) and the corresponding daily averaged TAN concentration (mgN/l) measured from effluent samples.

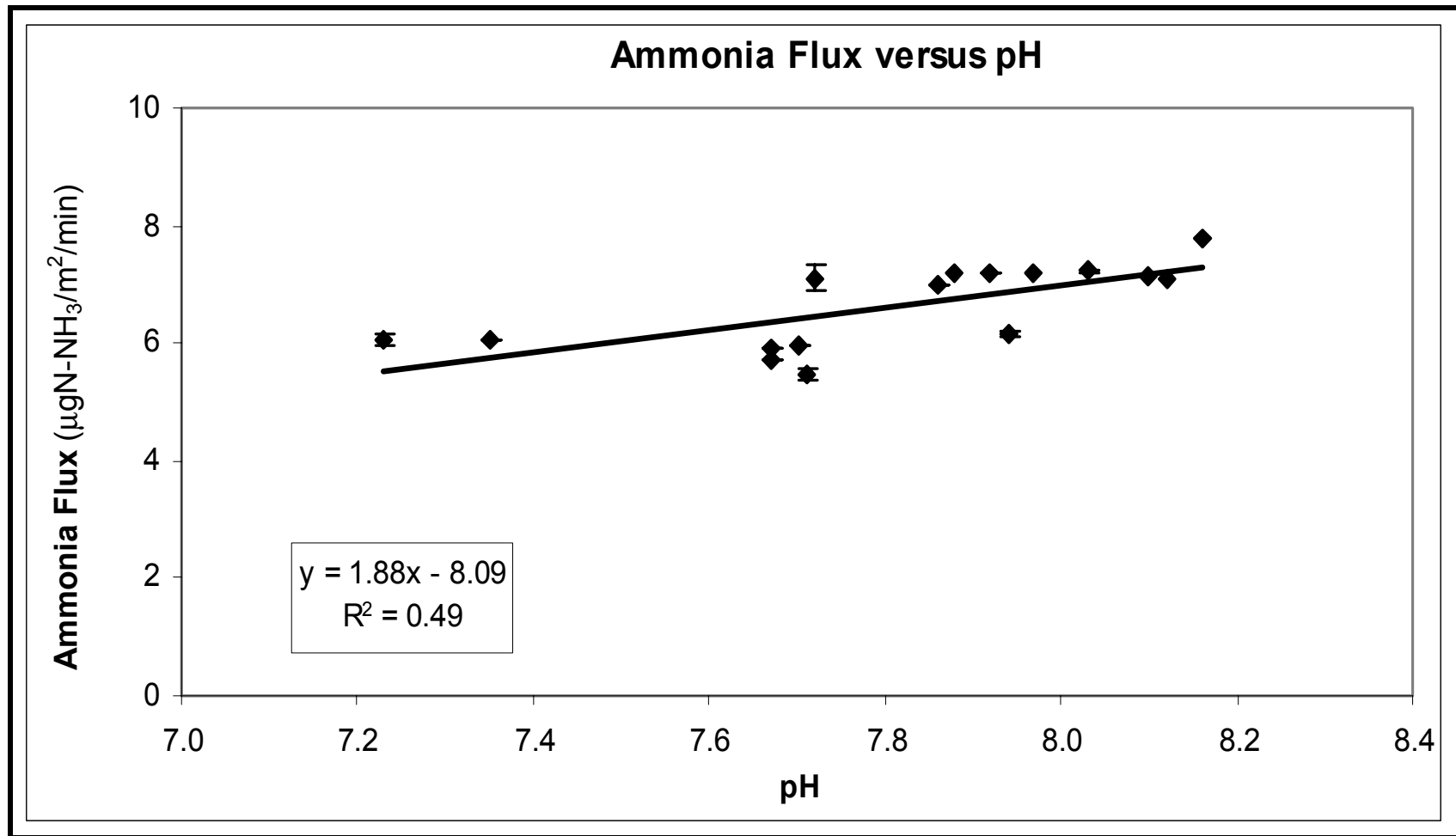


Figure 2.10 Ammonia Flux Versus Effluent pH. Each data point consists of a daily averaged ammonia flux measurement ($\mu\text{gN-NH}_3/\text{m}^2/\text{min}$) and the corresponding daily averaged pH measured from effluent samples.

Ammonia Flux versus Effluent Temperature and TAN Concentration

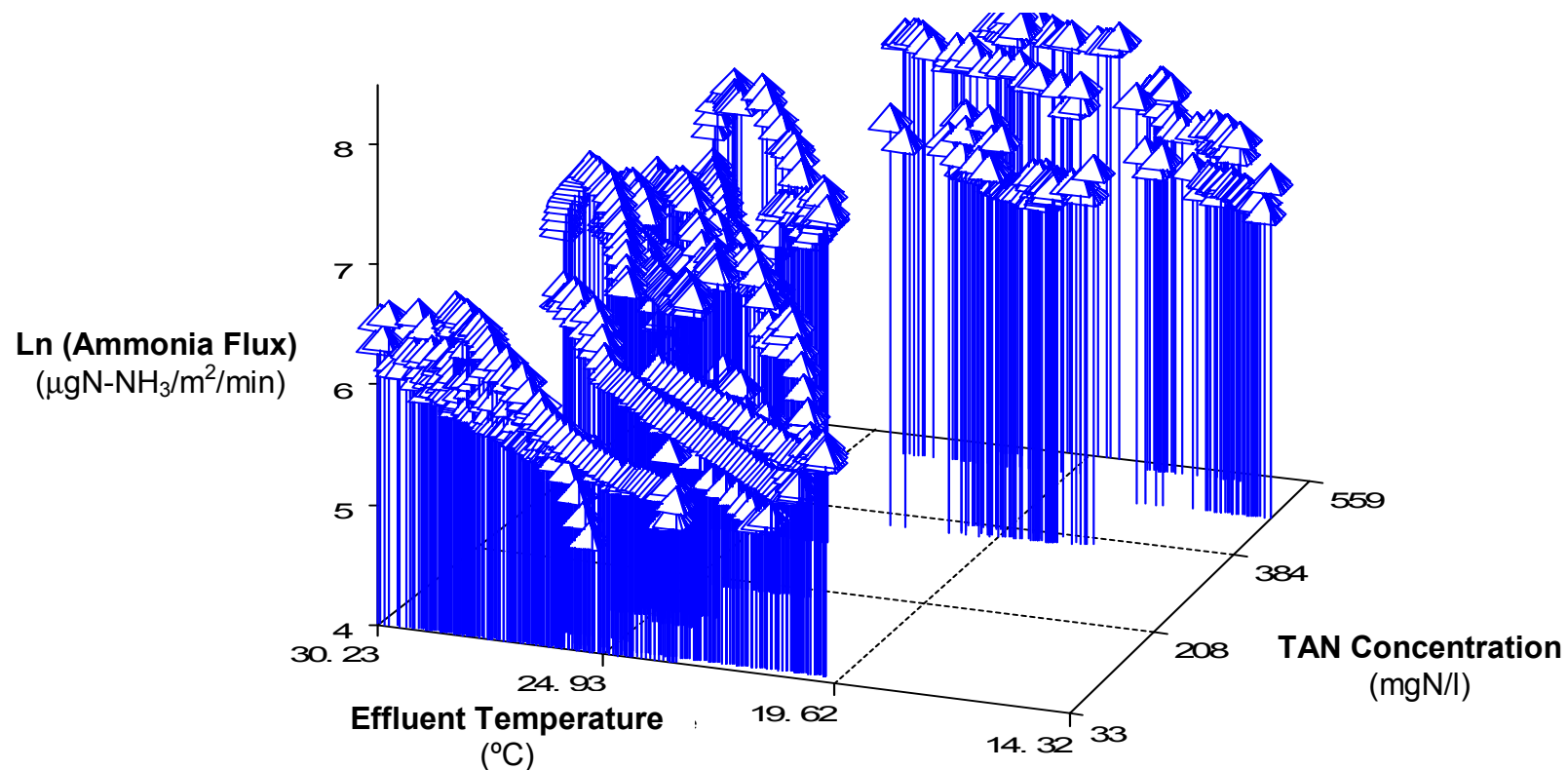


Figure 2.11 Ammonia Flux Versus Effluent Temperature and TAN Concentration from Barham Farm and Howard Farm. Each data point consists of a 15 minute averaged ammonia flux measurement, the corresponding 15 minute averaged lagoon temperature reading, and the TAN concentration measured from a corresponding lagoon sample.

Ammonia Flux versus Effluent Temperature and pH

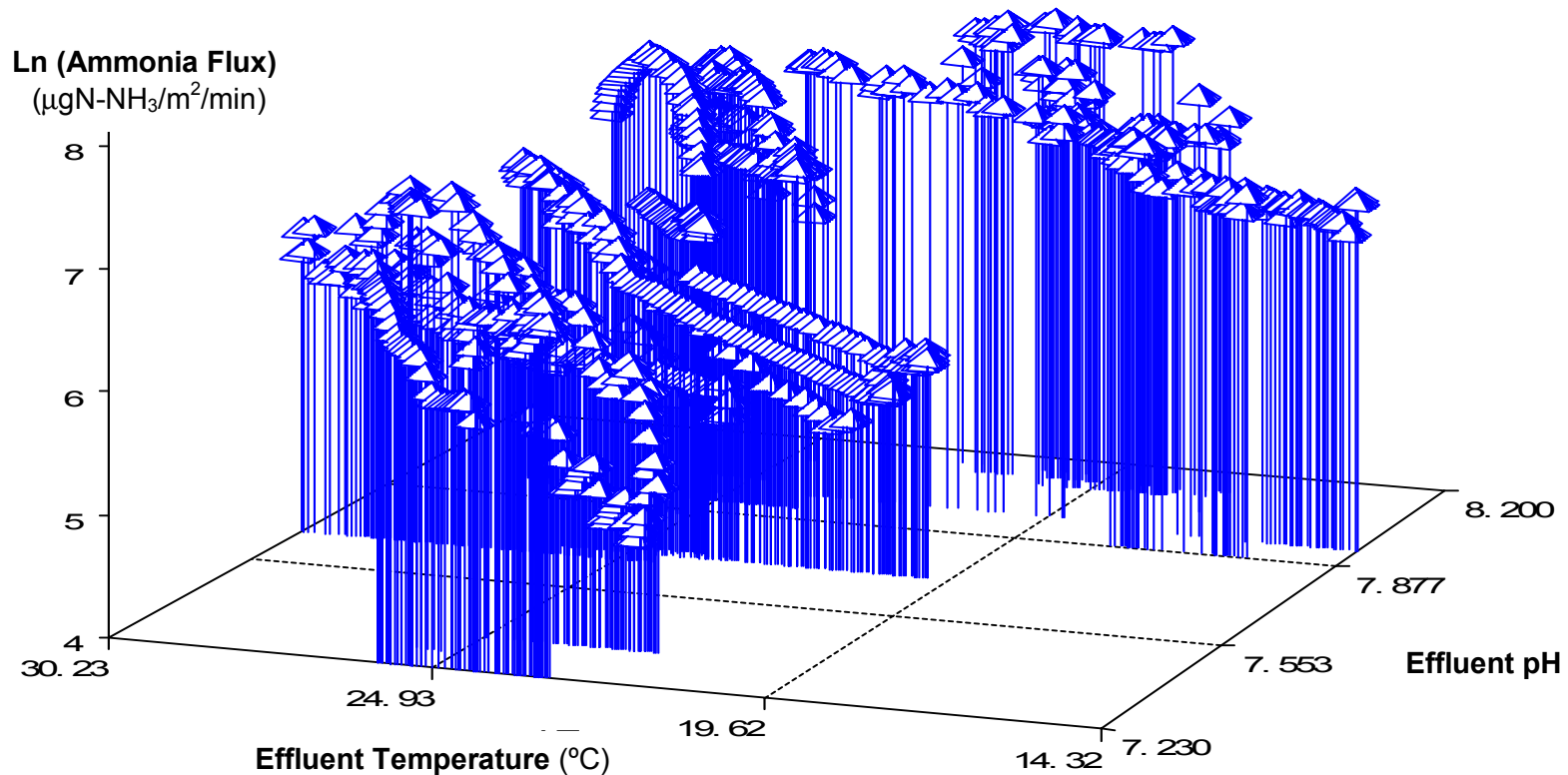


Figure 2.12 Ammonia Flux Versus Effluent Temperature and pH from Barham Farm and Howard Farm. Each data point consists of a 15 minute averaged ammonia flux measurement, the corresponding 15 minute averaged lagoon temperature reading, and the pH measured from a corresponding lagoon sample.

CHAPTER III. SIMULATION OF AMMONIA FLUX ACROSS A GAS-LIQUID INTERFACE VIA A COUPLED MASS TRANSFER WITH CHEMICAL REACTIONS MODEL

Abstract

A coupled mass transfer with chemical reactions model for ammonia flux across a gas-liquid interface predicts ammonia emissions from hog waste treatment lagoons. The two-layer model incorporates lagoon temperature, lagoon pH, wind speed, air temperature, ambient ammonia concentration, and Total Ammoniacal Nitrogen (TAN) concentration as input parameters. A sensitivity analysis of the model reveals an exponential increase in the model's output, ammonia flux, with lagoon temperature and lagoon pH, and an approximately linear increase with lagoon TAN concentration and wind speed. Ammonia flux measurements made via the dynamic flow-through chamber system and associated data taken from nine hog waste treatment lagoons located in eastern North Carolina are incorporated into a comparative analysis between measured and modeled ammonia fluxes. The ammonia flux output by the coupled model reproduces 65% of the average hourly variation in the ammonia flux measurements. Modeled ammonia fluxes reflect the general diurnal pattern exhibited by the measured ammonia fluxes.

Introduction

Atmospheric ammonia (NH_3) contributes to environmental processes such as aerosol formation and aquatic eutrophication. In the atmosphere, ammonia combines with acidic species and expedites the formation of particulates (Finlayson-Pitts, 1986). With a relatively short atmospheric residence time of approximately 1 to 5 days, any remaining gaseous ammonia quickly deposits onto earth's surfaces (Warneck, 2000). Ammonia that deposits onto aquatic ecosystems augments the existing nitrogen load, potentially creating a state of eutrophication in areas such as coastal waters (Paerl, 1995).

Domestic animal waste contributes the largest amount of ammonia to the global atmospheric budget. Ammonia emissions in the state of North Carolina have recently garnered much attention, due to the dramatic increase in the state's hog population and associated waste treatment facilities (Figure 1.2). Reduction in ammonia emissions could mitigate some of the negative effects of atmospheric ammonia, yet before reduction strategies are determined or implemented, scientists must first quantitatively assess the various sources and deposition processes of atmospheric ammonia. Through a combination of field measurements and theoretical modeling studies, scientists have investigated ammonia emissions associated with agricultural activities in order to determine appropriate emission factors.

Traditionally in North Carolina, commercial hog operations utilize lagoon and spray technology for animal waste treatment. In this type of system, the waste is broken down and stored in primary, secondary and tertiary anaerobic waste treatment lagoons and is ultimately sprayed on adjacent crop land as fertilizer. Measurements of ammonia flux from traditional and experimental hog waste treatment lagoons (Aneja et al., 2001a;

Aneja et al., 2000) and from fertilized and unfertilized soils (Roelle and Aneja, 2001) have been collected and analyzed with respect to corresponding meteorological and chemical parameters, including lagoon and soil temperature, pH, and Total Ammoniacal Nitrogen (TAN). TAN equals the total concentration of ammonia and ammonium (NH_4^+) within the liquid effluent.

Previous studies have investigated theoretical models that describe the flux of ammonia from domestic animal waste. Jayaweera and Mikkelsen (1990) have constructed a model to predict ammonia volatilization from flooded soil systems that incorporates TAN, pH, temperature, floodwater depth and wind speed. Ammonia volatilization from manure pits in swine buildings has also been investigated. The model established for this process relies on parameters such as manure temperature and air velocity (Zhang et al., 1994). Westerman et al. (1999) have created a model for ammonia flux from anaerobic swine waste lagoons that takes into account liquid pH, temperature, wind speed and TAN. De Visscher et al. (2002) have expanded on that two layer model. The model accounts for the aqueous equilibrium reaction of ammonia and ammonium, the adsorption of ammonium on suspended organic material, and the diffusive transfer of ammonia and ammonium across liquid and air boundary layers. The model incorporates effluent concentration, water temperature, wind speed, and effluent pH. The model simulates ammonia emissions measured via micrometeorological techniques (Harper and Sharpe, 1998) and explains 70% of the variation observed in daily averaged ammonia flux measurements (De Visscher et al., 2002).

Aneja et al. (2001b) have developed a coupled mass transfer with chemical reactions model that describes ammonia flux across a swine waste lagoon-air interface.

This two layer model takes into account the equilibrium reaction of ammonia and ammonium in solution, the pseudo-first order reaction of ammonia with acidic species in the atmosphere, and the molecular transfer of ammonia across liquid and gas films on either side of the interface. The model incorporates air temperature, lagoon temperature, lagoon pH, wind speed, TAN, and ambient ammonia concentration, all of which are monitored during field campaigns. The modeled ammonia flux exhibits an exponential increase with lagoon temperature and pH and a linear increase with wind speed and TAN (Aneja et al., 2001b).

This study compares ammonia flux measurements made from traditional and experimental hog waste treatment lagoons (Aneja et al., 2001a; Aneja et al., 2000) to the output of the coupled mass transfer with chemical reactions model (Aneja et al., 2001b). Data from ten field campaigns that took place at nine different hog waste treatment lagoons located in eastern North Carolina are included in the comparative analysis. By simultaneously evaluating modeled and measured ammonia flux with respect to corresponding environmental parameters, discrepancies can be established and analyzed, highlighting characteristics of the model or the measurements that require attention. In this manner, this study strives to quantitatively assess ammonia flux from hog waste treatment lagoons via a combination of modeling and measurements in order to advance the development of emission reduction strategies and sustainable agricultural operations.

Materials and Methods

Field Measurements

Dynamic Chamber System

A dynamic chamber system with continuous impeller stirring (Figure 1.6) (Aneja et al., 2001a; Aneja et al., 2000; Kim et al., 1994; Kaplan et al., 1988) is used to measure ammonia flux from waste treatment lagoon and other liquid effluent surfaces at commercial hog operations in eastern North Carolina. The system consists of a four foot by four foot floating plywood platform and a plastic cylindrical chamber. The translucent chamber fits into a circular hole cut in the center of the platform and penetrates the lagoon surface by approximately 8 cm. The seal formed between the bottom of the cylinder and the lagoon water ensures a closed system inside the chamber. Fluorinated ethylene propylene (FEP) Teflon lines the entire inner surface of the chamber. The chamber has a diameter of 25.4 cm, an internal height of 45.72 cm, and a volume of 23,167 cm³.

A carrier gas of compressed air flows through the system at variable rates, and a mass flow controller adjusts and records the flow rates to a datalogger system. A variable speed Teflon impeller keeps the air within the chamber ideally mixed. The entire closed system consists of Teflon tubing, Teflon lining or stainless steel fittings in order to minimize chemical reactions with sample stream. A vent on the sample line exiting the chamber prevents the system from over pressurizing. The vent is periodically bubble tested during sampling periods to check for under pressurization or leaks in the system.

Once the system reaches steady state conditions, the sample line is connected to a Thermo Environmental Instruments (TECO) Model 17c chemiluminescence ammonia

analyzer in order to quantify the concentration of ammonia within the sample stream exiting the chamber. The ammonia analyzers are located in a mobile laboratory contained within a modified Ford Aerostar van. The van has a 13,500 BTU air conditioning unit that regulates the climate for effective performance of the ammonia analyzers. Calibration of the ammonia analyzers is performed using certified standard mixtures of nitric oxide and ammonia, zero grade air, and a Thermo Environmental Instruments 146 dilution/titration instrument. A multipoint calibration of the ammonia analyzers is conducted in the laboratory prior to each measurement campaign. Zero and span checks occur approximately every other day during field campaigns, and the multipoint calibration is rechecked at the conclusion of each measurement period.

Ammonia Flux Calculation

The following steady-state mass balance expression (Equation 3.1) describes the chemical and physical dynamics within the flow-through chamber system used to quantify ammonia flux for this study.

$$J = \left[(L) \left(\frac{2}{r} + \frac{1}{h} \right) + \frac{q}{V} \right] (C)(h) \quad (3.1)$$

J represents the ammonia flux as an area source in dimensions of mass per area per time. The carrier gas flow rate, q, the chamber dimensions, height, h, radius, r, and volume, V, and the steady state ammonia concentration, C, are measured directly. The loss term, L, describes the loss of ammonia to the chamber walls and is determined experimentally based on the method of Kaplan et al. (1988).

Environmental Parameters

Effluent temperature and pH are monitored by a Campbell Scientific Instruments 107 temperature probe and an Innovative sensors pH probe. The sensors monitor the

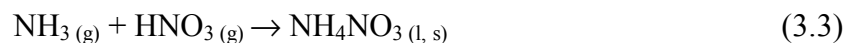
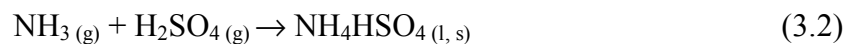
temperature and pH of the effluent at a depth of approximately 15 cm adjacent to the dynamic chamber system during ammonia flux measurement periods. Daily lagoon water samples are taken adjacent to the dynamic chamber system as it measures ammonia flux and are submitted to a laboratory in the Biological and Agricultural Engineering Department at North Carolina State University for analysis of TAN. A meteorological tower contains air temperature and wind speed sensors that monitor the ambient conditions. Ambient ammonia concentration is also measured during ammonia flux measurement periods, via Fourier Transform Infrared Radiation (FTIR) spectroscopy, annular denuder or chemiluminescence ammonia analyzers.

Coupled Mass Transfer with Chemical Reactions Model

Based on the quiescent thin film concept (Danckwerts, 1970), the mechanistic model includes a thin gas film extending from the air-liquid interface to the well-mixed region of the air and a thin liquid film extending from the air-liquid interface to the well-mixed region of the liquid (Figure 1.10). The well-mixed regions of air and liquid are referred to as the bulk gas and liquid phases and are assumed to be of indeterminate height. Molecular diffusion and chemical reactions are accounted for as transport mechanisms in both films (Aneja et al., 2001b).

Gas Phase Dynamics

The model includes the gas phase chemical reactions of ammonia with sulfuric acid, nitric acid, hydrochloric acid, and the hydroxyl radical (OH), illustrated in the following equations.





The following basic diffusion equation (Equation 3.6) governs the concentration gradient of ammonia in the gas film.

$$D_a \left(\frac{d^2 C}{dz^2} \right) = K_a(C) \quad (3.6)$$

D_a represents the diffusivity of ammonia in the gas phase, and K_a equals the pseudo first order reaction rate of ammonia in the gas phase, calculated by assuming constant concentrations of sulfuric acid, nitric acid, hydrochloric acid, and the hydroxyl radical (Malik, 1999). C represents the concentration of gaseous ammonia at height z in the gas film.

The solution to the basic diffusion equation using the following boundary conditions (Equation 3.7) describes the concentration of ammonia with respect to height within the gas film.

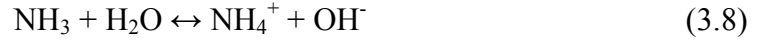
$$\begin{aligned} z = 0; C(0) &= C_{ai} \\ z = t_a; C(t_a) &= C_a \end{aligned} \quad (3.7)$$

C_{ai} equals the gas phase concentration of ammonia at the gas-liquid interface. t_a represents thickness of the liquid film. C_a represents the concentration of ammonia in the bulk gas phase, which equals the ambient ammonia concentration, for the model assumes a well-mixed bulk gas phase of undefined height. The flux of ammonia to the atmosphere is directly proportional to the negative ammonia concentration gradient in the gas film. The transport of ammonia in the gas phase relies on such parameters as the effective first order reaction rate constant, the gas phase diffusion coefficient for ammonia, ambient ammonia concentration, and the gas phase mass transfer coefficient of

ammonia, which has been parameterized with respect to wind speed (Mackay and Yeun, 1983). These parameters ultimately rely on air temperature and wind speed.

Liquid Phase Dynamics

The equilibrium reaction of ammonia and ammonium (Equation 3.8) dictates the transport of ammonia in the liquid film.



The following component material balance (Equation 3.9) underlies the dynamics of the model in the liquid film. It encompasses molecular transport within the liquid film and corresponds to the liquid phase equilibrium reaction between ammonia and ammonium (Olander, 1960).

$$D_L \left(\frac{d^2 C_L}{dz^2} \right) + D_L' \left(\frac{d^2 C_L'}{dz^2} \right) = 0 \quad (3.9)$$

D_L and C_L represent the diffusivity and concentration of ammonia, and D_L' and C_L' represent the diffusivity and concentration of ammonium. The concentrations of ammonia and ammonium in the liquid phase depend on pH and TAN concentration, and the liquid phase diffusivities of ammonia and ammonium depend on temperature and viscosity.

The solution to the component material balance equation describes the concentration of ammonia with respect to height in the liquid film. The flux of ammonia to the liquid is directly proportional to the negative ammonia concentration gradient in the liquid film. Olander (1960) has applied the following boundary conditions (Equation 3.10) in order to define the expression for ammonia flux to the liquid film.

$$\begin{aligned} z = 0; C(0) &= C_{Li} \\ z = t_L; C(t_L) &= C_L \end{aligned} \quad (3.10)$$

The resulting equation for ammonia flux to the liquid film is as follows (Equation 3.11).

$$J_L = \left(\frac{D_L}{t_L} \right) (C_{Li} - C_L) \left(1 + (D'_L / D_L) K \right) \quad (3.11)$$

J_L denotes the flux of ammonia to the liquid film. C_{Li} and C_L equal the concentration of ammonia at the air-liquid interface and in the bulk liquid phase, respectively. C_L is based on the TAN concentration of the liquid. K equals the ratio of ammonium concentration to ammonia concentration, which depends on the equilibrium reaction rate (Zhang, 1998) and the pH of the liquid. t_L represents the thickness of the liquid film and equals the ratio of the liquid phase diffusivity of ammonia to the liquid phase mass transfer coefficient of ammonia, which has been parameterized with respect to wind speed (Mackay and Yeun, 1983). The transport of ammonia in the liquid phase relies on such parameters as the equilibrium reaction rate, the liquid phase diffusion coefficient for ammonia and ammonium, and the liquid phase mass transfer coefficient of ammonia. These parameters ultimately rely on effluent temperature, pH, TAN, and wind speed.

Net Ammonia Flux

At the interface, the ammonia flux to the gas phase equals the negative of the ammonia flux to the liquid phase. For equilibrium conditions at the interface, Henry's Law relates the gas and liquid phase concentrations of ammonia, as illustrated in Equation 3.12.

$$HC_{Li} = C_{ai} \quad (3.12)$$

H equals the Henry's Law constant for ammonia, as defined by Dasgupta and Dong (1986). C_{Li} and C_{ai} are the concentrations of ammonia in the liquid and gas phases at the interface, respectively. By setting the ammonia flux to the gas phase equal to the

negative ammonia flux to the liquid phase and by utilizing Henry's Law, the following expression for net ammonia flux across the interface is obtained (Equation 3.13).

$$J = \frac{(D_a r_a) \{HC_L (A + 1/A) - 2C_a\}}{(A - 1/A) \{1 + H(A + 1/A)(B)\}} \quad (3.13)$$

In which

$$B = \frac{D_a r_a t_L}{D_L (A - (1/A)) (1 + (D'_L / D_L) K)} \quad (3.14)$$

J equals the net flux of ammonia across the gas-liquid interface and has dimensions of mass per area per time. D_a represents the diffusivity of ammonia in the gas phase. A equals $e^{r_a t_a}$, in which r_a equals $\sqrt{K_a / D_a}$ and K_a represents the first order reaction rate constant for ammonia in the gas phase. The thickness of the gas and liquid films are denoted by t_a and t_L . D_L and D'_L denote the diffusivities of ammonia and ammonium in the liquid phase. C_a and C_L equal the concentration of ammonia in the bulk gas and liquid phases. H represents the Henry's Law constant, and K equals the ratio of ammonia and ammonium in the liquid phase.

The net ammonia flux output by the coupled model describes the flux of ammonia to the atmosphere across the surface of a waste treatment lagoon. In the model, ammonia flux ultimately depends on lagoon temperature, lagoon pH, wind speed, lagoon TAN concentration, air temperature and ambient ammonia concentration. Measurements of these parameters occur in conjunction with ammonia flux measurements during field campaigns. Thus, measured ammonia fluxes may be compared to corresponding ammonia fluxes output by the coupled model.

Results and Discussion

A sensitivity analysis reveals the individual effect of each input parameter on the model's output, ammonia flux. Lagoon temperature, lagoon pH, wind speed, and lagoon TAN concentration significantly affect the magnitude of the modeled ammonia flux, while air temperature and ambient ammonia concentration affect the model's output to a lesser extent. The responses of the modeled flux to individual variations in each of the six variables have been investigated.

Lagoon Temperature and Ammonia Flux

Henry's Law coefficient, the liquid phase diffusivity of ammonia and ammonium, the dissociation constant, and the viscosity and density of the liquid layer all directly depend on lagoon temperature. Lagoon temperatures measured during ammonia flux measurement periods range from 1.51°C to 38.41°C. The modeled ammonia flux increases exponentially in response to a variation of lagoon temperature from 0°C to 40°C, with the other variables held constant at values typically observed from swine waste treatment lagoons. Figure 3.1 illustrates the resulting increase in ammonia flux from 149 $\mu\text{gN-NH}_3/\text{m}^2/\text{min}$ to 7,859 $\mu\text{gN-NH}_3/\text{m}^2/\text{min}$.

The exponential dependence of ammonia flux on lagoon temperature follows from the increase of the Henry's Law coefficient, the liquid phase diffusivity of ammonia and ammonium, and the dissociation constant with lagoon temperature. The liquid phase mass transfer coefficient of ammonia relies on the liquid phase diffusivity of ammonia and on the viscosity and density of the liquid. An increase in lagoon temperature leads to a decrease in the viscosity and density of the liquid and an increase in the diffusivity of ammonia. The mass transfer coefficient consequently increases with lagoon temperature.

Lagoon pH and Ammonia Flux

The pH of a waste treatment lagoon dictates the fraction of ammonia that exists in solution, in accordance with the following equilibrium reaction (Equation 3.15).



An increase in pH leads to an increase in hydroxide (OH⁻) concentration, which consequently shifts the equilibrium to the left. An increase in the fraction of ammonia in solution ensues. The lagoon pH measured during ammonia flux measurement campaigns ranges from 6.60 to 8.47. The modeled ammonia flux increases exponentially in response to an increase in pH from 6.5 to 8.5, with the other variables held constant. Figure 3.2 illustrates the exponential increase in ammonia flux from 34 µgN-NH₃/m²/min to 4,625 µgN-NH₃/m²/min.

The exponential increase of modeled ammonia flux with pH occurs due to the dependence of ammonia concentration on hydroxide concentration in the liquid solution, for pH is a logarithmic function of hydroxide concentration. The pH of the liquid dictates the distribution of TAN between ammonia and ammonium, and hence determines the fraction of TAN that exists as ammonia in solution. The modeled ammonia flux directly depends on the fraction of ammonia in solution, as the magnitude of the ammonia flux is proportional to the difference in ammonia concentrations between the bulk liquid and gas phases.

Total Ammoniacal Nitrogen and Ammonia Flux

The effluent in a typical anaerobic hog waste lagoon ultimately breaks down into methane, carbon dioxide, and amines. The carbon dioxide and methane readily volatilize to the atmosphere, while the amines break down into ammonia, which remains in solution

for a longer period of time due to its relatively high solubility. In solution, ammonia dissociates into ammonium, and the equilibrium reaction between these two compounds ultimately dominates the chemistry of the waste lagoon. The Total Ammoniacal Nitrogen (TAN) concentration in a waste lagoon equals the total concentration of both ammonia and ammonium in the effluent. During ammonia flux measurement periods, the lagoon TAN concentrations ranged from 29.6 mgN/l to 1786.7 mgN/l. A change in TAN from 0 mgN/l to 1800 mgN/l with the other variables held constant results in a linear increase of modeled flux from $-24 \mu\text{gN-NH}_3/\text{m}^2/\text{min}$ to $4024 \mu\text{gN-NH}_3/\text{m}^2/\text{min}$, as illustrated in Figure 3.3.

In the coupled model, the ammonia concentration in the bulk liquid phase is directly proportional to the TAN concentration of the bulk liquid phase. The modeled ammonia flux is directly proportional to the ammonia concentration in the bulk liquid phase. Thus, the modeled ammonia flux is directly proportional to the TAN concentration of the bulk liquid phase, and consequently increases linearly with an increase in TAN concentration.

Wind Speed and Ammonia Flux

Wind speeds measured during ammonia flux measurement periods range from 0.00 m/s to 11.31 m/s. A change in wind speed from 0 m/s to 10 m/s with the other variables held constant results in an approximately linear increase in modeled ammonia flux from $323 \mu\text{gN-NH}_3/\text{m}^2/\text{min}$ to $7,412 \mu\text{gN-NH}_3/\text{m}^2/\text{min}$, as illustrated in Figure 3.4. Wind speed affects the modeled ammonia flux via the mass transfer coefficients of ammonia in the gas and liquid phases. Along with the gas and liquid phase diffusivities

of ammonia, the mass transfer coefficients determine the thickness of the gas and liquid films.

Mackay and Yeun (1983) have parameterized the mass transfer coefficients of various gaseous species with respect to friction velocity, which in turn has been parameterized with respect to 10 m wind speed. Each mass transfer coefficient is related to a specific gaseous compound via the Schmidt Number, which equals the ratio of the kinematic viscosity of a medium to the diffusivity of the gaseous compound within that medium. According to the parametric equations utilized in the model, the gas phase mass transfer coefficient is a linear function of friction velocity, while the liquid phase mass transfer coefficient is a power function of friction velocity, which in turn is a power function of wind speed. Overall, an increase in wind speed results in an approximately linear increase in modeled ammonia flux.

Air Temperature and Ammonia Flux

The Henry's Law constant, the gas-phase diffusivity of ammonia, and the viscosity and density of the air depend on air temperature. Air temperature measurements range from -3.37 °C to 35.92 °C during ammonia flux measurement periods. A change in air temperature from -5°C to 35°C with the other variables held constant leads to a slight decrease in ammonia flux from 1223 $\mu\text{gN-NH}_3/\text{m}^2/\text{min}$ to 1048 $\mu\text{gN-NH}_3/\text{m}^2/\text{min}$. Figure 3.5 illustrates the trend in the modeled ammonia flux with the increase in air temperature.

The gas phase diffusivity of ammonia increases with an increase in air temperature, while the density of air and the Henry's Law constant decrease with an increase in air temperature. The influence of air temperature on the density and viscosity

of air affects the gas phase mass transfer coefficient of ammonia. The thickness of the gas film therefore depends on air temperature, through interactions with both the gas phase diffusivity and the gas-phase mass transfer coefficient of ammonia. Overall, air temperature affects the thickness of the gas film and the equilibrium between the gas and liquid phase ammonia concentrations at the interface, leading collectively to a slight decrease in modeled ammonia flux with an increase in air temperature.

Ambient Ammonia Concentration and Ammonia Flux

The modeled ammonia flux directly depends on ambient ammonia concentration, as the flux is proportional to the difference between the ammonia concentrations in the bulk gas and liquid phases. The ambient ammonia concentration measurements made during ammonia flux measurement periods range from 10 ppb to 952 ppb. Varying the ambient ammonia concentration from 0 ppb to 700 ppb while holding the other variables constant causes a slight decrease in modeled ammonia flux from 1124 $\mu\text{gN-NH}_3/\text{m}^2/\text{min}$ to 955 $\mu\text{gN-NH}_3/\text{m}^2/\text{min}$, as illustrated in Figure 3.6.

For situations involving waste treatment lagoon-air interfaces, an increase in ambient ammonia concentration generally decreases the difference in ammonia concentration between the bulk gas and liquid phases, for the concentration of ammonia in the bulk liquid phase generally exceeds that in the bulk gas phase. Thus, the modeled ammonia flux slightly decreases due to an increase in ambient ammonia concentration, with the other variables held constant at typical values observed from a hog waste treatment lagoon. The linear nature of the slight decrease follows from the direct dependence of modeled ammonia flux on the difference in concentration of ammonia between the bulk gas and liquid phases. Ambient ammonia concentration affects the

model only slightly because the concentration of ammonia in the bulk liquid phase greatly exceeds that in the gas phase for values typically observed at a hog waste treatment lagoon. Thus, changes in ambient ammonia concentration have far less of an effect on the model's output than changes in the liquid ammonia concentration does.

Measured and Modeled Ammonia Flux

A comparative analysis between measured and modeled ammonia fluxes elucidates the effectiveness of the model. Measurements of hourly-averaged lagoon temperature, lagoon pH, wind speed, lagoon TAN concentration, air temperature, and ambient ammonia concentration that directly correspond to the ammonia flux measurements are input into the coupled mass transfer model in order to perform the comparative analysis. The analysis includes ammonia flux measurements and corresponding modeled ammonia fluxes from three studies, encompassing ten field campaigns that took place at hog waste treatment lagoons located in eastern North Carolina.

The first study includes data collected during August of 1997 through May 1998 from a primary waste lagoon at a commercial hog operation in Sampson County, North Carolina. The study incorporates data from four seasons at the same lagoon in order to highlight seasonal patterns (Aneja et al., 2000). Data from the summer and spring seasons are included in the comparative analysis. The second study incorporates six lagoons located at four farms in eastern North Carolina in order to assess potential differences in ammonia emissions from primary, secondary and tertiary waste lagoons. The study includes data collected from September 1998 through March 1999 (Aneja et al., 2001a). Data from all six lagoons are included in this comparative analysis. The last

two farms in the analysis are part of the Odor, Pathogens and Emissions of Nitrogen (OPEN) Program.

Program OPEN incorporates 18 farms across the state of North Carolina, all of which currently employ experimental waste treatment technologies that potentially reduce emissions of odor, pathogens and nitrogen compounds, specifically ammonia. Barham Farm, located near Zebulon, North Carolina, utilizes a covered anaerobic waste treatment lagoon in order to trap pollutants such as methane and carbon dioxide. Ammonia flux measurements made in early April 2002 from a secondary waste lagoon, referred to as the storage pond and overflow pond, adjacent to the covered lagoon are included in this comparative analysis. At Howard Farm, located near Richlands, North Carolina, a constructed wetland processes waste. After flowing through a solid-separator, the waste flows through the constructed wetland cells, where vegetation uptakes nutrients from the liquid effluent. Ammonia flux measurements made in June 2002 from four locations along the wetland cells and from a secondary waste lagoon, referred to as the finishing pond, are included in this comparative analysis.

Figure 3.7 illustrates the mean modeled and measured ammonia fluxes from the ten field campaigns. The magnitude of ammonia flux varies significantly between the field campaigns. The figure illustrates the coupled mass transfer model's ability to approximate the magnitude of a range of ammonia flux measurements. Table 3.1 lists the average values of the lagoon temperature, lagoon pH, lagoon TAN, and wind speed measurements from each field campaign, and Table 3.2 lists the average values of the measured and modeled ammonia flux from each field campaign. For the cases in which the coupled model overestimates measurements of ammonia flux, the field campaigns

tend to have relatively high lagoon pH and TAN concentrations. In the coupled model, lagoon pH and TAN dictate the concentration of ammonia in the bulk liquid phase, which in turn dictates the level of ammonia flux, for the modeled ammonia flux is proportional to the difference between ammonia concentrations in the bulk liquid and gas phases. Thus, a combination of lagoon pH and lagoon TAN concentration dictates the level of ammonia emissions from an individual lagoon. The large variation in ammonia flux between field campaigns seemingly stems from differences in lagoon pH and lagoon TAN concentration. Changes in lagoon temperature due to seasonal variation can also manifest differences in ammonia flux between field campaigns.

Figure 3.8 summarizes the modeled and measured fluxes from the field campaigns by study. In the figure, the overall comparison combines the three studies and therefore includes all ammonia flux data from hog waste treatment lagoons in eastern North Carolina collected using the dynamic chamber system. This figure illustrates the coupled mass transfer model's accuracy in predicting the level of measured ammonia flux from an overall study.

In order to assess the daily variability of the modeled and measured ammonia fluxes, average diurnal profiles of ammonia flux from each study are illustrated in Figures 3.9, 3.10, and 3.11. The pattern and magnitude of the calculated ammonia fluxes closely resemble those of the observed ammonia fluxes. For each of the three studies, the model underestimates the observed ammonia fluxes during nighttime hours and overestimates the observed ammonia fluxes during daytime hours. The distinct diurnal pattern suggests that the model may overemphasize a variable with a distinct diurnal pattern, such as lagoon temperature or wind speed as illustrated in Figure 3.12 and Figure

3.13. The effects of both wind speed and lagoon temperature can enhance the diurnal variation of modeled ammonia flux.

Figure 3.14 presents a regression of modeled ammonia flux on measured ammonia flux for the overall data set. Each data point represents hourly data points averaged over the duration of each field campaign. The model's output accounts for 66% of the variation in measured ammonia fluxes. Figure 3.14 also highlights the nearly one to one ratio between the measured and modeled ammonia fluxes.

Conclusion

The coupled mass transfer with chemical reactions model (Aneja et al., 2001b) evaluated in this study outputs ammonia flux across a gas-liquid interface, and depends on lagoon temperature, lagoon pH, wind speed, lagoon TAN concentration, air temperature, and ambient ammonia concentration. Increases in lagoon temperature and pH lead to exponential increases in modeled ammonia flux, while increases in wind speed and TAN lead to approximately linear increases in modeled ammonia flux. Air temperature and ambient ammonia affect the model's output to a lesser extent than the other variables do. Lagoon pH and TAN concentration largely dictate the level of modeled ammonia flux, while lagoon temperature and wind speed affect the daily variability of modeled ammonia flux, for these two parameters tend to exhibit distinct diurnal patterns with maximum values occurring in the afternoon. The coupled mass transfer with chemical reactions model reproduces much of the variation in measured ammonia flux from each farm and from each study. Overall, the model encompasses 65% of the variability of hourly measured ammonia fluxes during the ten field campaigns, and the measured and modeled fluxes exhibit close to a one to one ratio.

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Table 3.1 Environmental Parameters from each Field Campaign.

Measurement Period	Lagoon Temperature (°C)	Lagoon pH	Wind Speed (m/s)	Lagoon TAN (mgN/l)
August 5-15, 1998	30.00±3.30	7.50±0.18	2.18±1.07	550.9±23.5
May 16-23, 1999	24.7±3.20	7.70±0.06	2.57±1.13	512.8±40.8
Aneja et al., 2000	28.48±3.49	7.59±0.10	2.36±1.11	531.9±23.5
September 15-23, 1998	23.27±3.00	7.78±0.36	1.35±1.09	177.7±34.8
October 6-17, 1998	19.49±6.68	6.95±0.18	0.86±0.1.02	73.8±4.0
November 5-15, 1998	10.94±3.50	7.40±0.35	1.18±1.33	435.4±10.4
November 19-27, 1998	13.24±1.18	7.06±0.28	0.93±0.98	483.7±0.0
March 1-9, 1999	10.31±1.32	7.47±0.40	3.41±2.52	576.2±4.0
March 19-27, 1999	18.88±0.2.22	6.83±0.07	1.61±1.20	1286.9±458.8
Aneja et al., 2001a	15.17±6.39	7.26±0.44	1.59±1.73	502.1±426.6
April 1-12, 2002	17.68±3.66	8.09±0.18	1.66±0.94	455±191
June 3-13, 2002	24.87±1.56	7.70±0.25	2.10±1.42	98±88
Program OPEN	22.85±4.20	7.80±0.29	1.99±1.32	209.8±186.3

Table 3.2 Comparative Analysis of Measured and Modeled Ammonia Fluxes.

Farm Location	Measurement Period	Lagoon Type	Measured Flux $\mu\text{gN-NH}_3/\text{m}^2/\text{min}$	Modeled Flux $\mu\text{gN-NH}_3/\text{m}^2/\text{min}$
Sampson County	Aug 1-15, 1997	Primary	3967±893	2784±1841
Sampson County	May 16-27, 1998	Primary	1842±501	3254±1559
Aneja et al., 2000	Overall	---	3255±1274	2941±1763
Raleigh	Sep 15-23, 1998	Primary	212±101	588±432
Raleigh	Oct 6-17, 1998	Secondary	146±74	14±17
Rocky Mount	Nov 5-15, 1998	Tertiary	114±31	75±55
Rocky Mount	Nov 19-25, 1998	Primary	140±27	67±35
Kenansville	Feb28-Mar9 1999	Primary	246±99	644±790
Warsaw	Mar 19-27, 1999	Primary	302±43	145±64
Aneja et al., 2001a	Overall	---	185±97	360±533
Zebulon	Apr 1-14, 2002	Storage Pond	1334±367	1877±1051
Richlands	Jun 3-13, 2002	Wetland	802±582	441±454
Program OPEN	Overall	---	918±585	755±868
All Farms	Overall	---	1483±1594	1395±1674

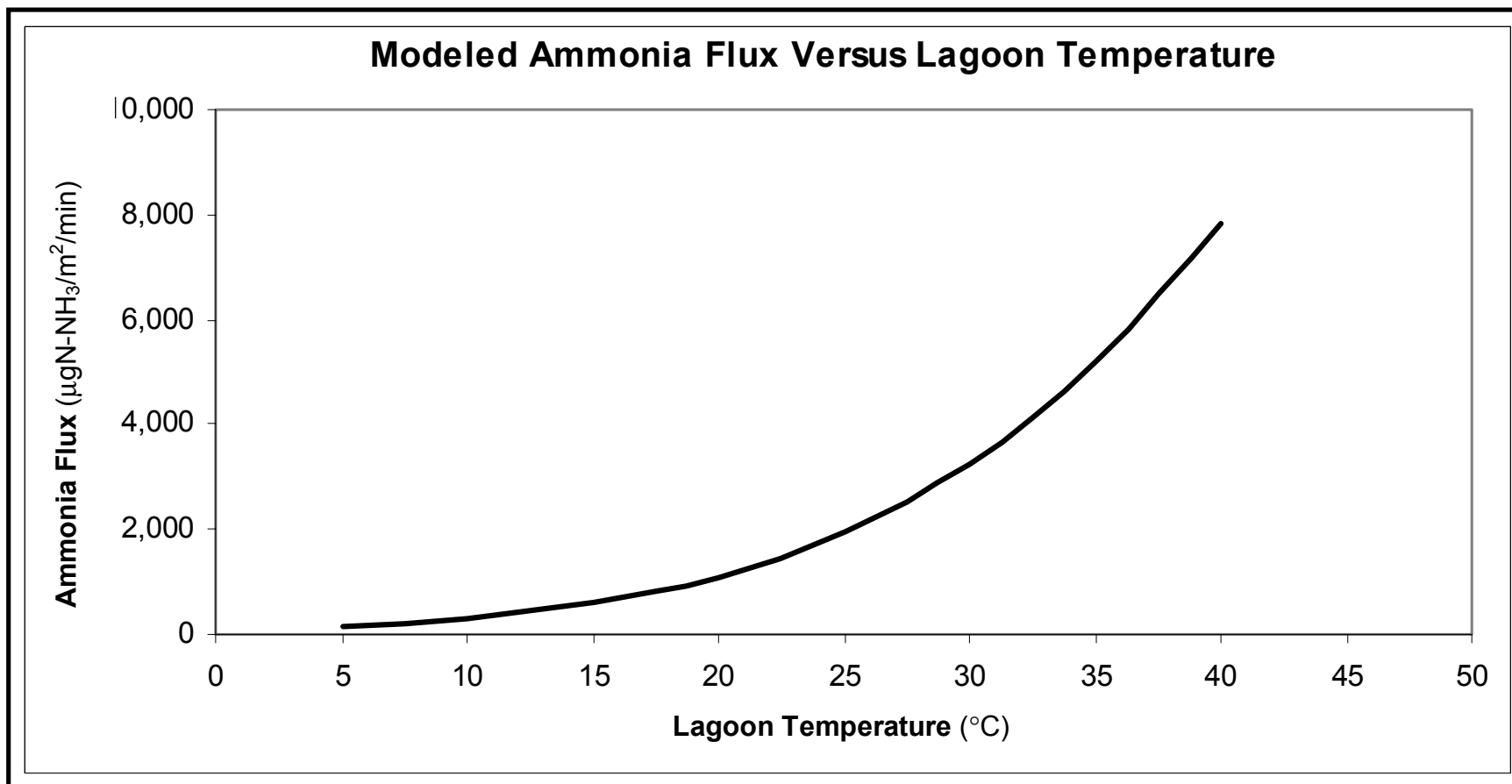


Figure 3.1 Modeled Ammonia Flux Versus Lagoon Temperature. Other model input parameters remain constant as follows, lagoon pH (7.8), wind speed (1.5 m/s), lagoon TAN concentration (500 mgN/l), air temperature (20°C), and ambient ammonia concentration (100 ppb).

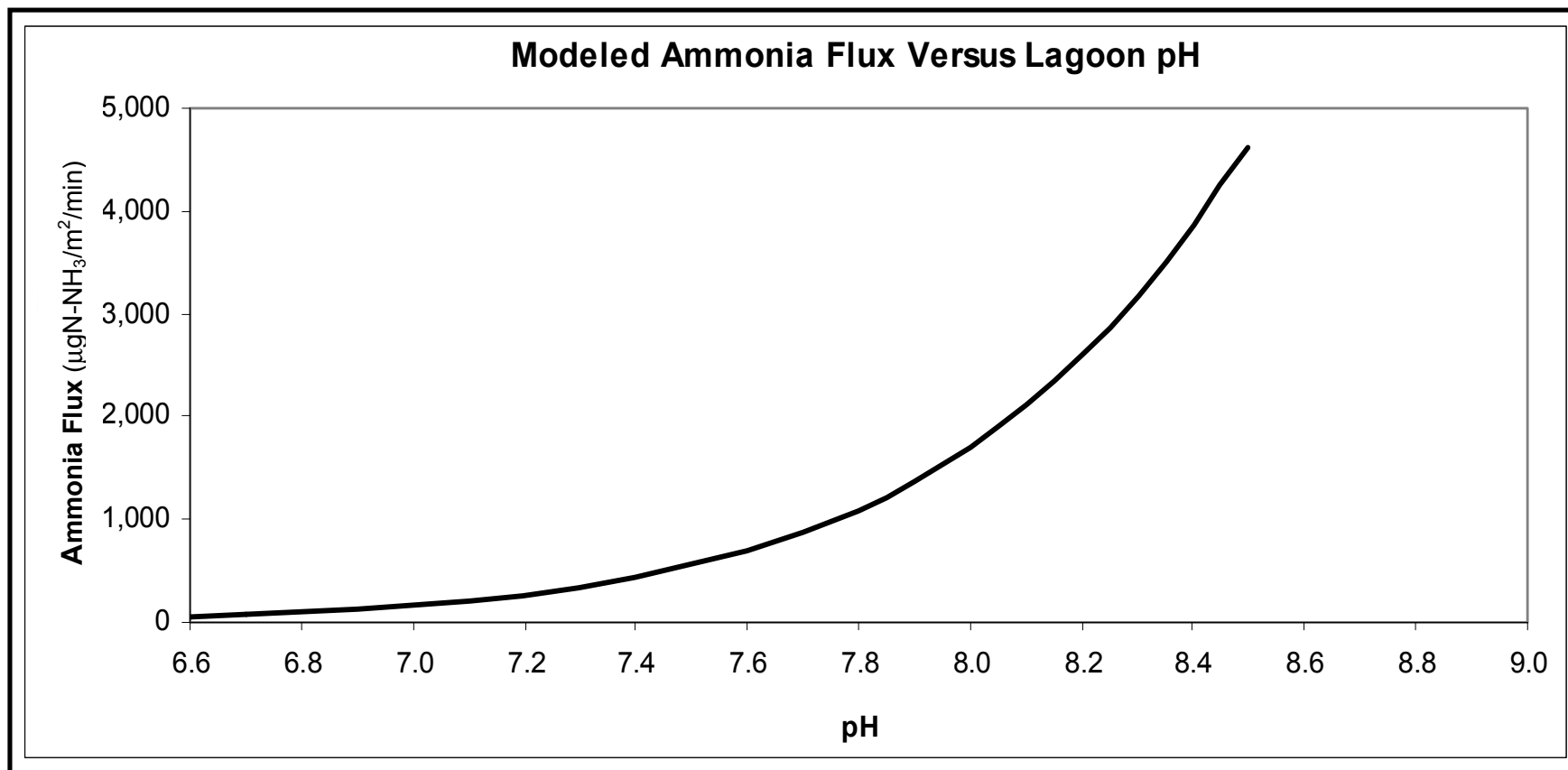


Figure 3.2 Modeled Ammonia Flux Versus Lagoon pH. Other model input parameters remain constant as follows, lagoon temperature (20°C), wind speed (1.5 m/s), lagoon TAN concentration (500 mgN/l), air temperature (20°C), and ambient ammonia concentration (100 ppb).

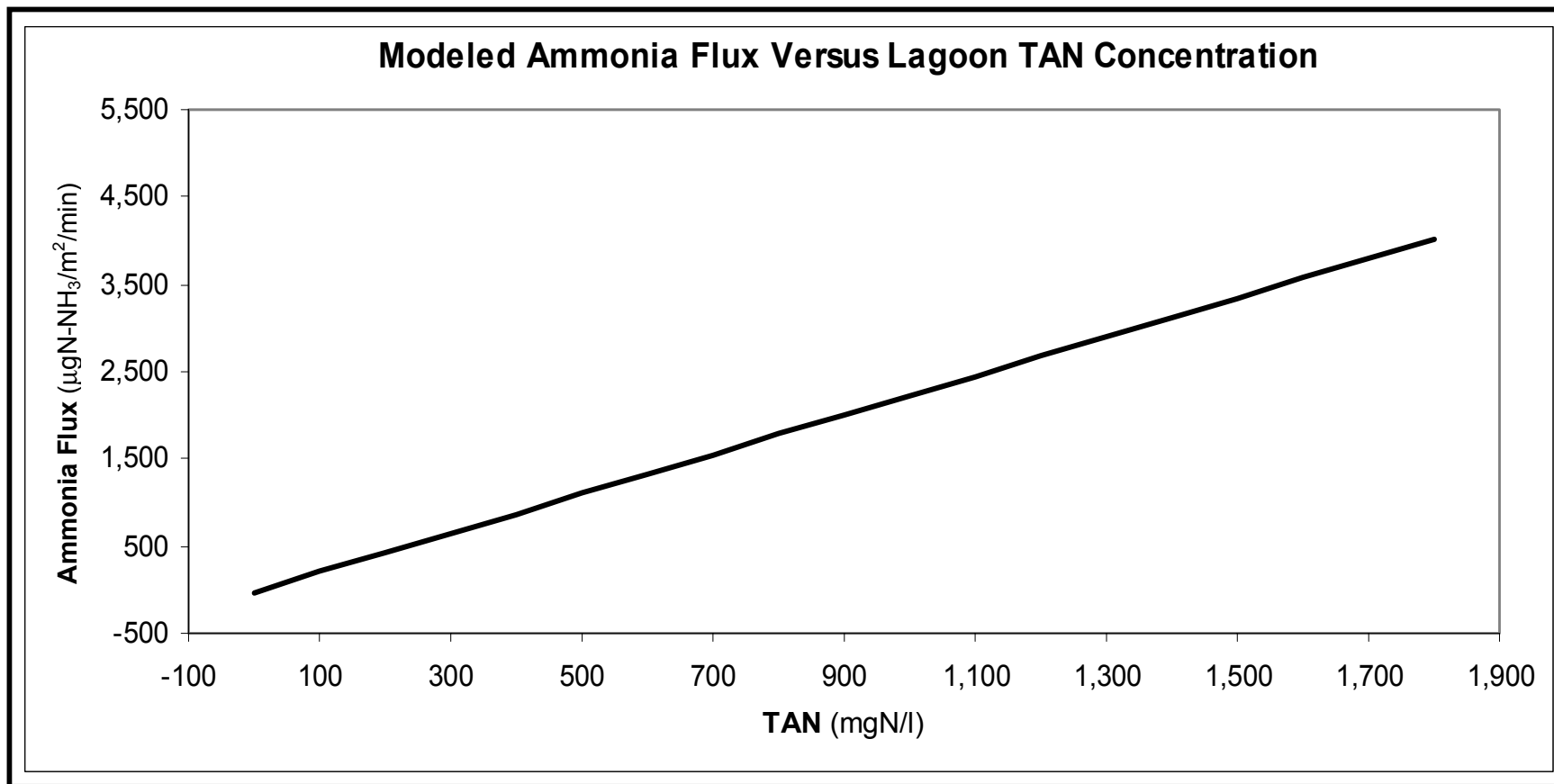


Figure 3.3 Modeled Ammonia Flux Versus Lagoon TAN Concentration. Other model input parameters remain constant as follows, lagoon temperature (20°C), wind speed (1.5 m/s), lagoon pH (7.8), air temperature (20°C), and ambient ammonia concentration (100 ppb).

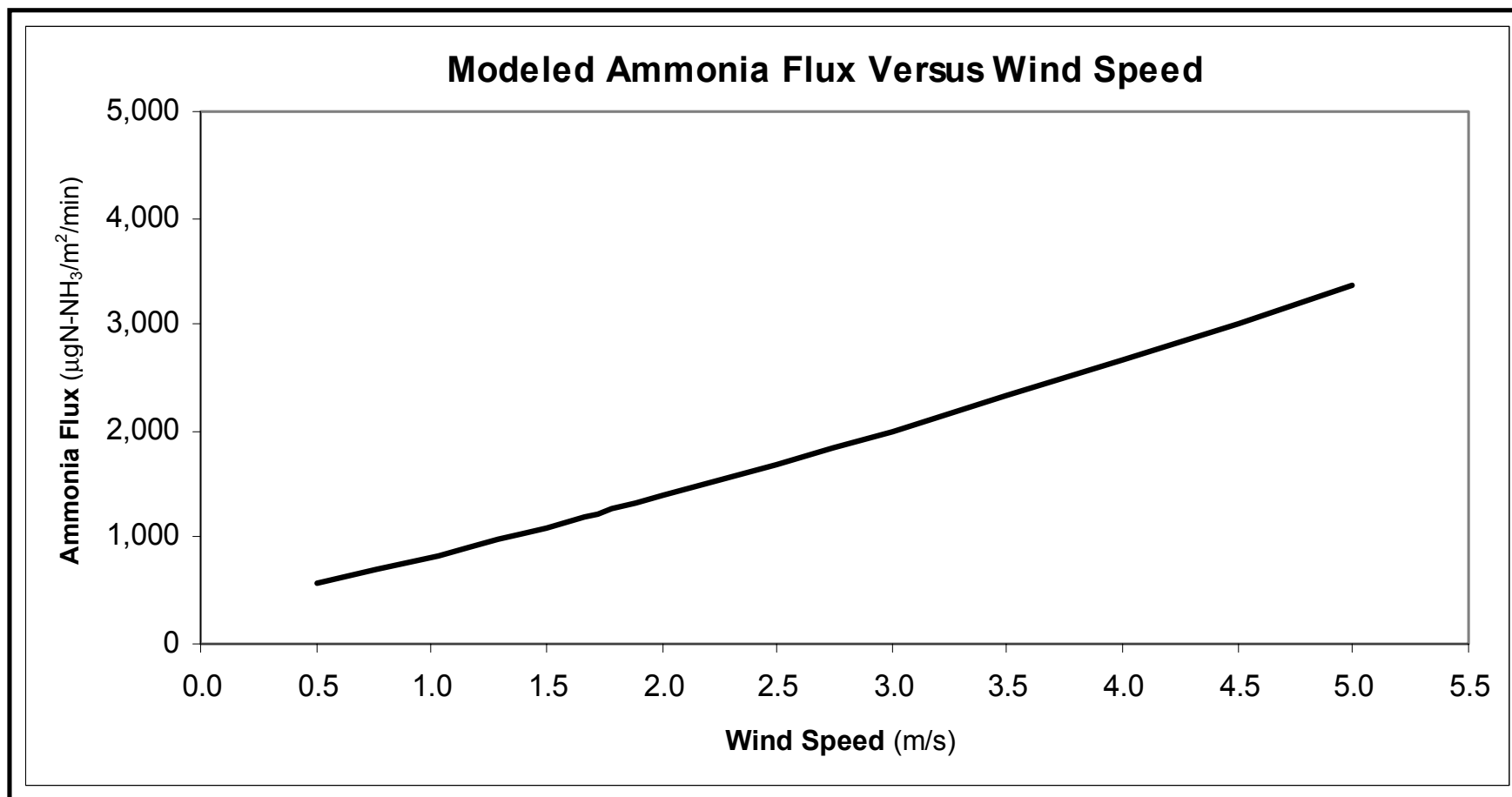


Figure 3.4 Modeled Ammonia Flux Versus Wind Speed. Other model input parameters remain constant as follows, lagoon temperature (20°C), lagoon TAN concentration (500 mgN/l), lagoon pH (7.8), air temperature (20°C), and ambient ammonia concentration (100 ppb).

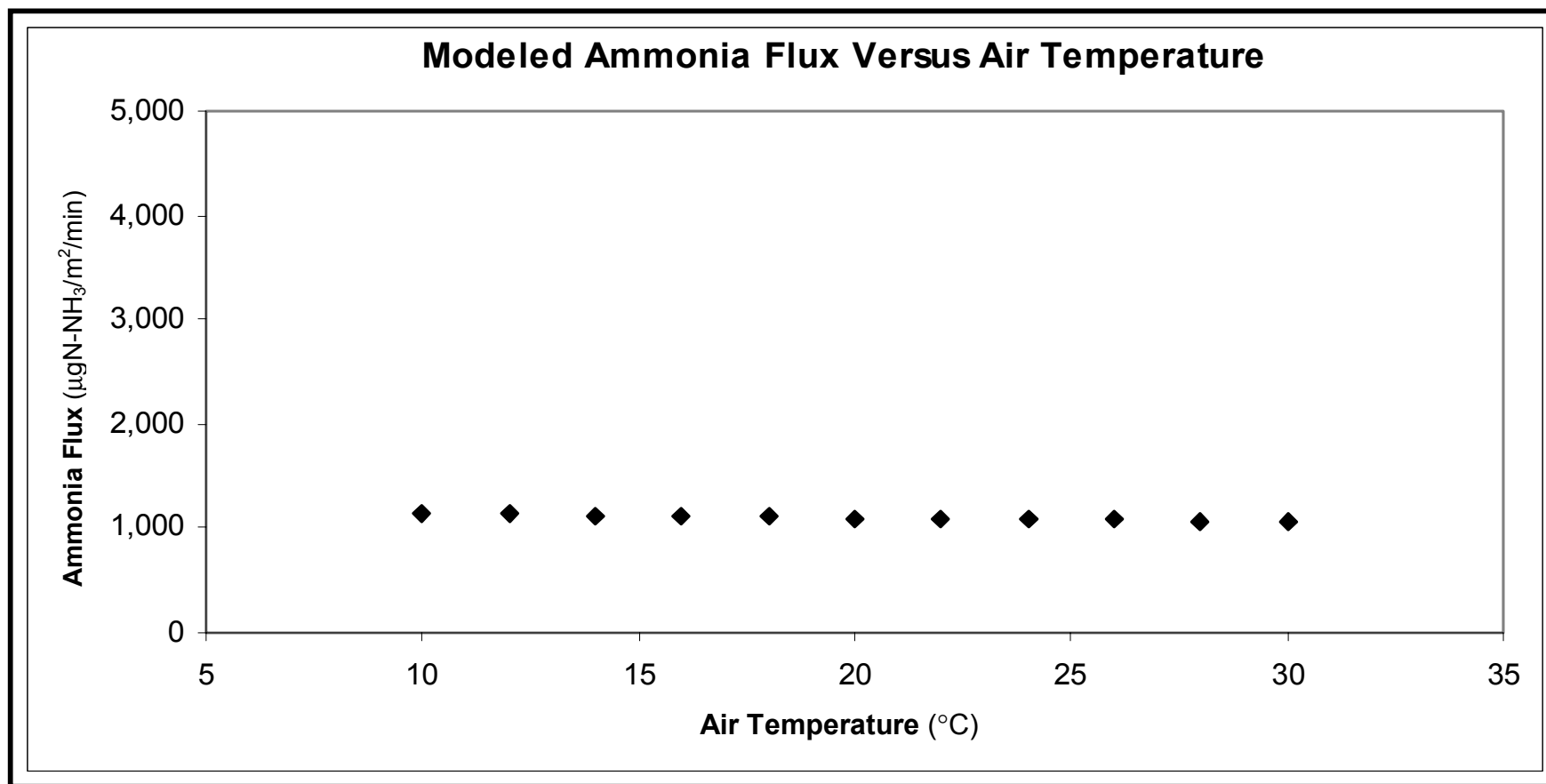


Figure 3.5 Modeled Ammonia Flux Versus Air Temperature. Other model input parameters remain constant as follows, lagoon temperature (20°C), lagoon TAN concentration (500 mgN/l), lagoon pH (7.8), wind speed (1.5 m/s), and ambient ammonia concentration (100 ppb).

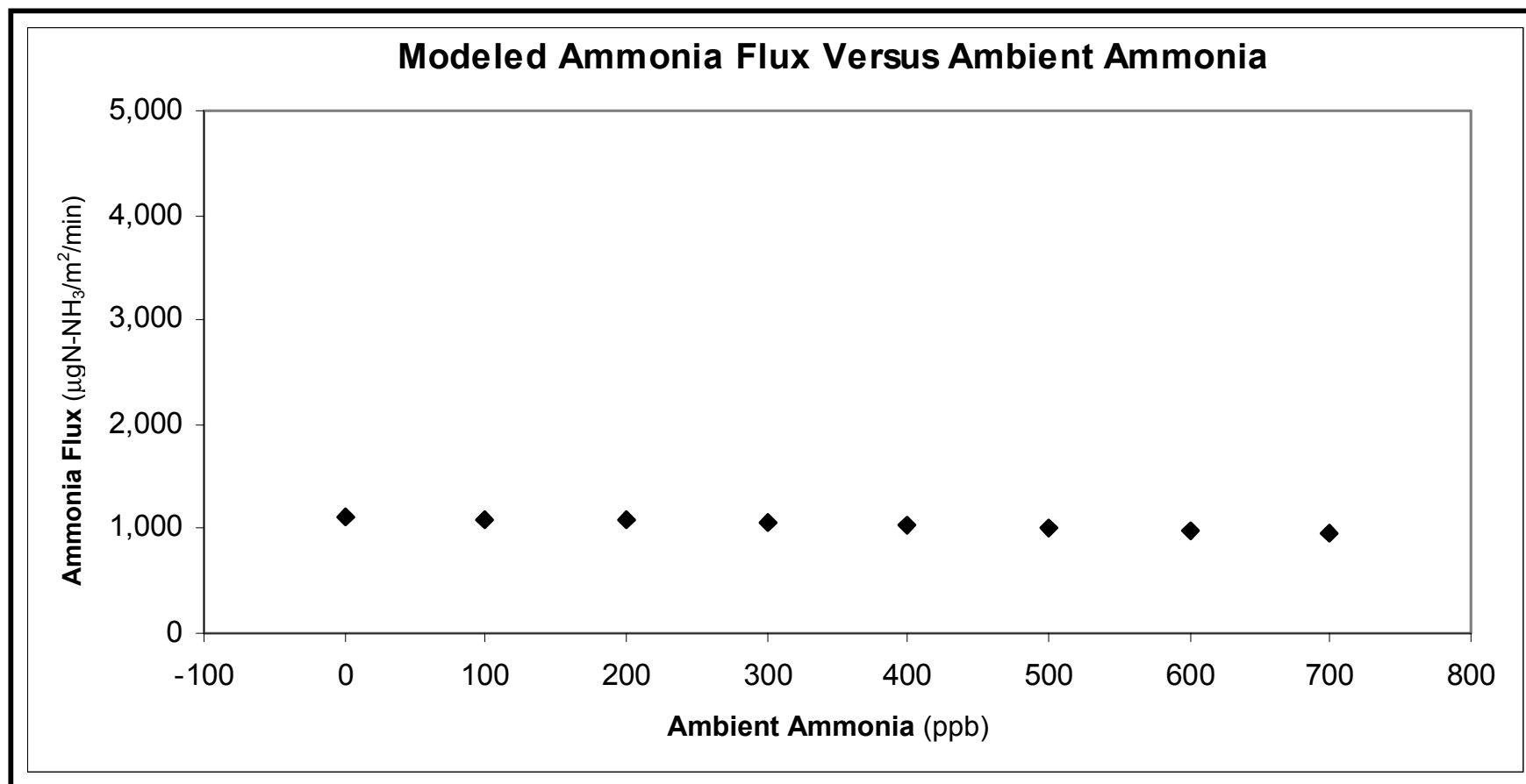


Figure 3.6 Modeled Ammonia Flux Versus Ambient Ammonia Concentration. Other model input parameters remain constant as follows, lagoon temperature (20°C), lagoon TAN concentration (500 mgN/l), lagoon pH (7.8), wind speed (1.5 m/s), and air temperature (20°C).

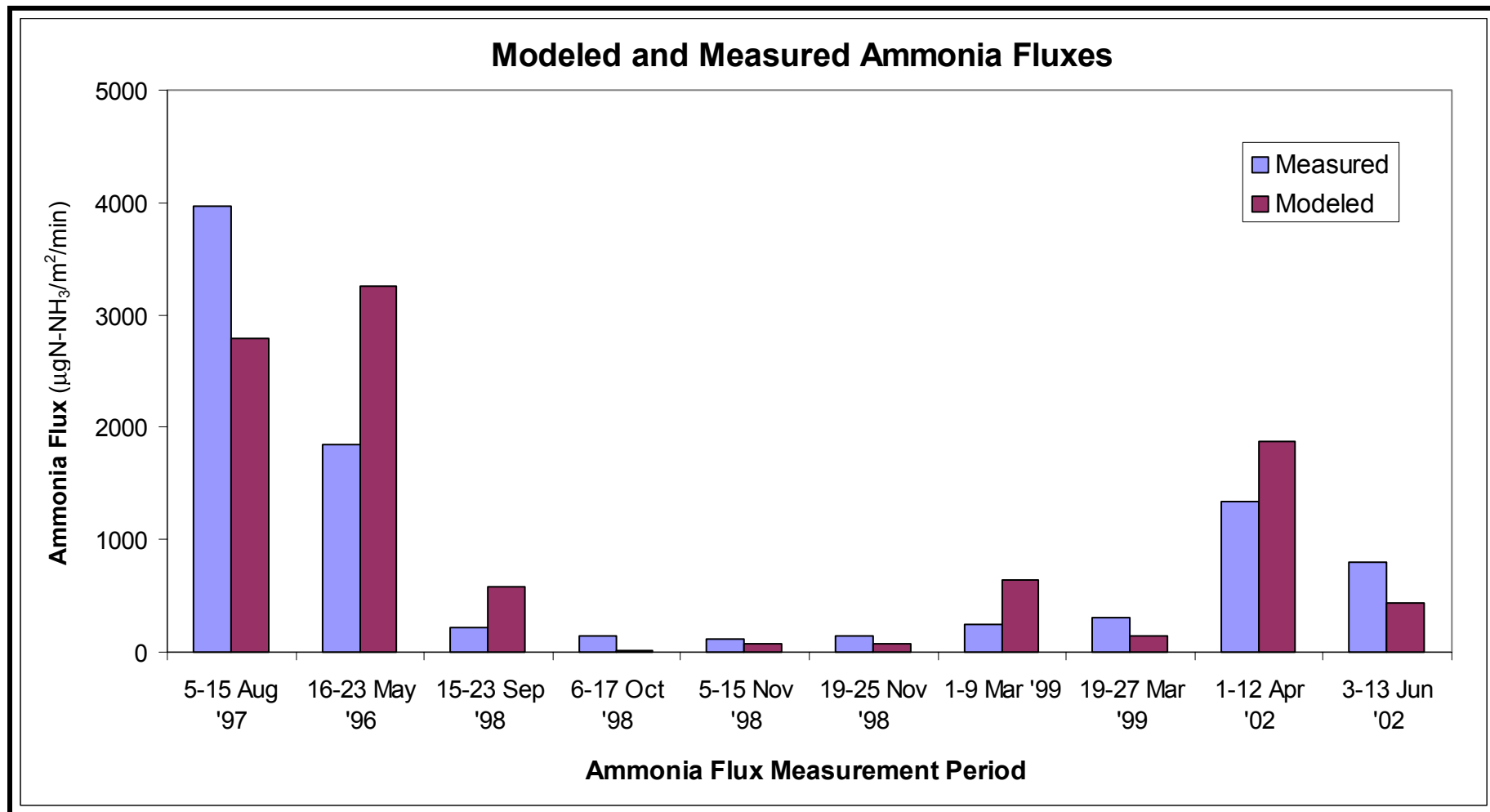


Figure 3.7 Average Modeled and Measured Ammonia Fluxes for each Field Campaign. Hourly averaged measurements of environmental parameters made during ammonia flux measurement periods are input into the Coupled Mass Transfer with Chemical Reactions Model in order to predict ammonia flux across the lagoon-air interface.

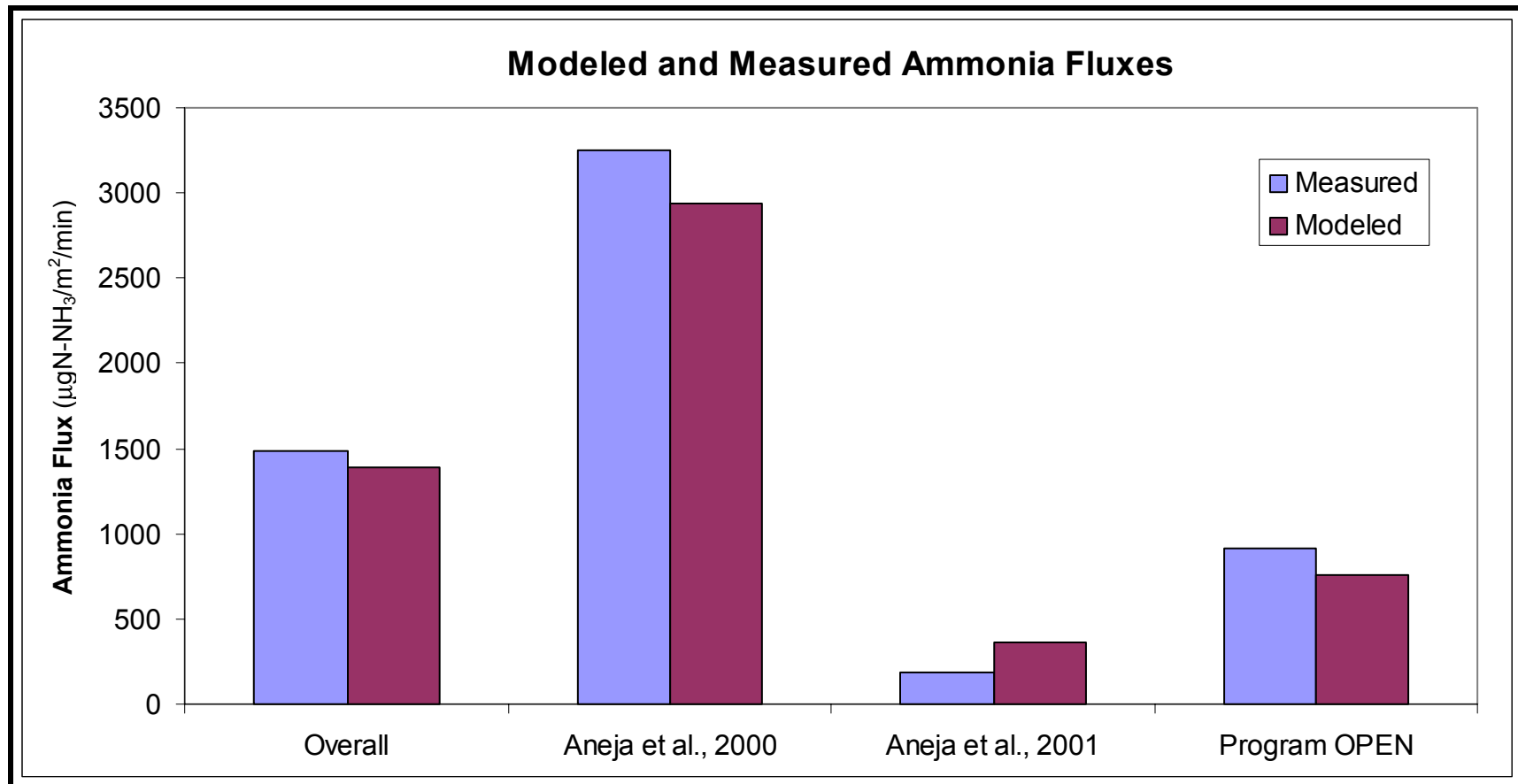


Figure 3.8 Average Modeled and Measured Ammonia Fluxes for each Study. The overall comparison includes all data from each of the three studies.

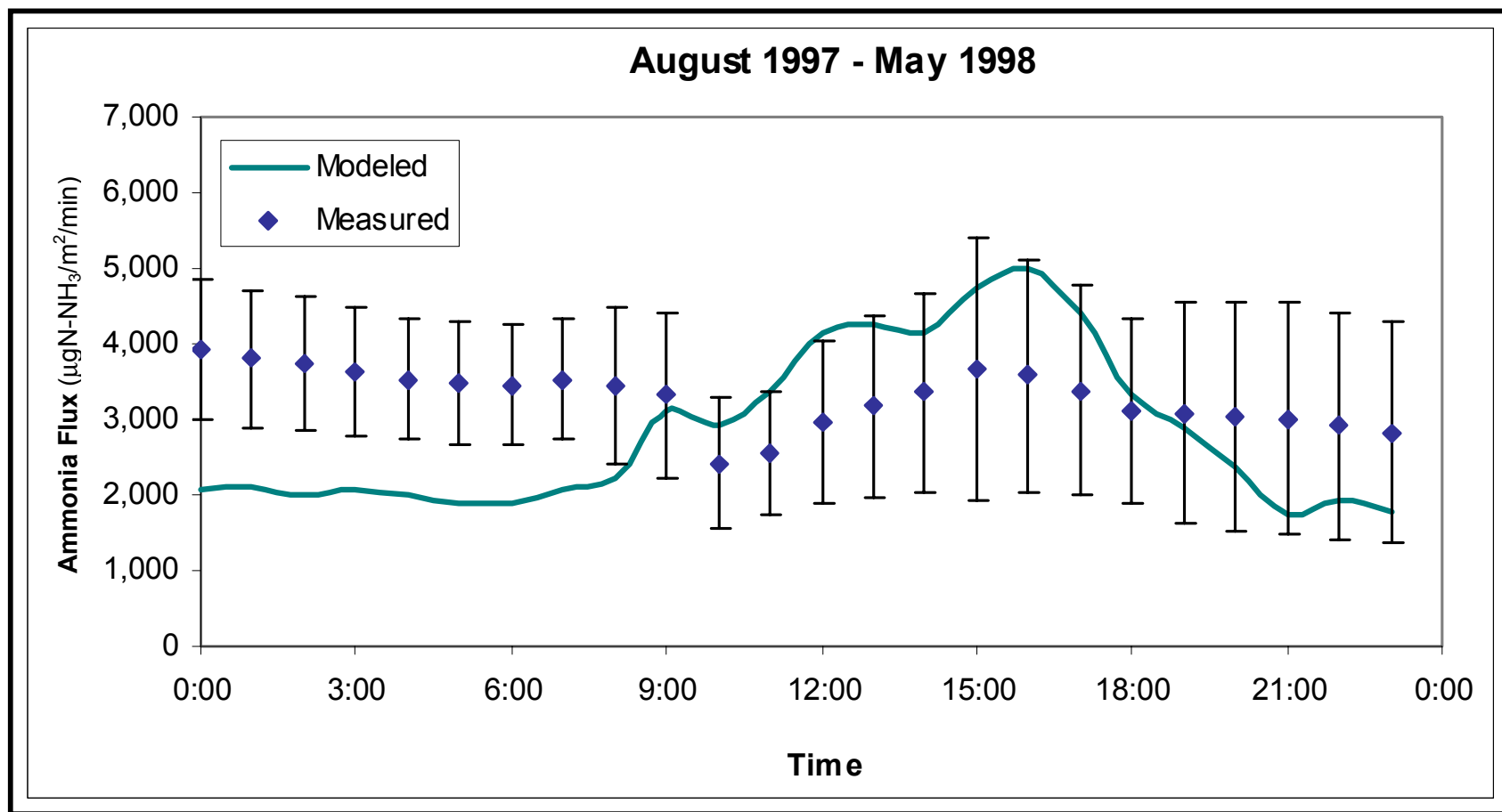


Figure 3.9 Diurnal Comparison of Measured and Modeled Ammonia Flux from August 1997 through May 1998 (Aneja et al., 2000).

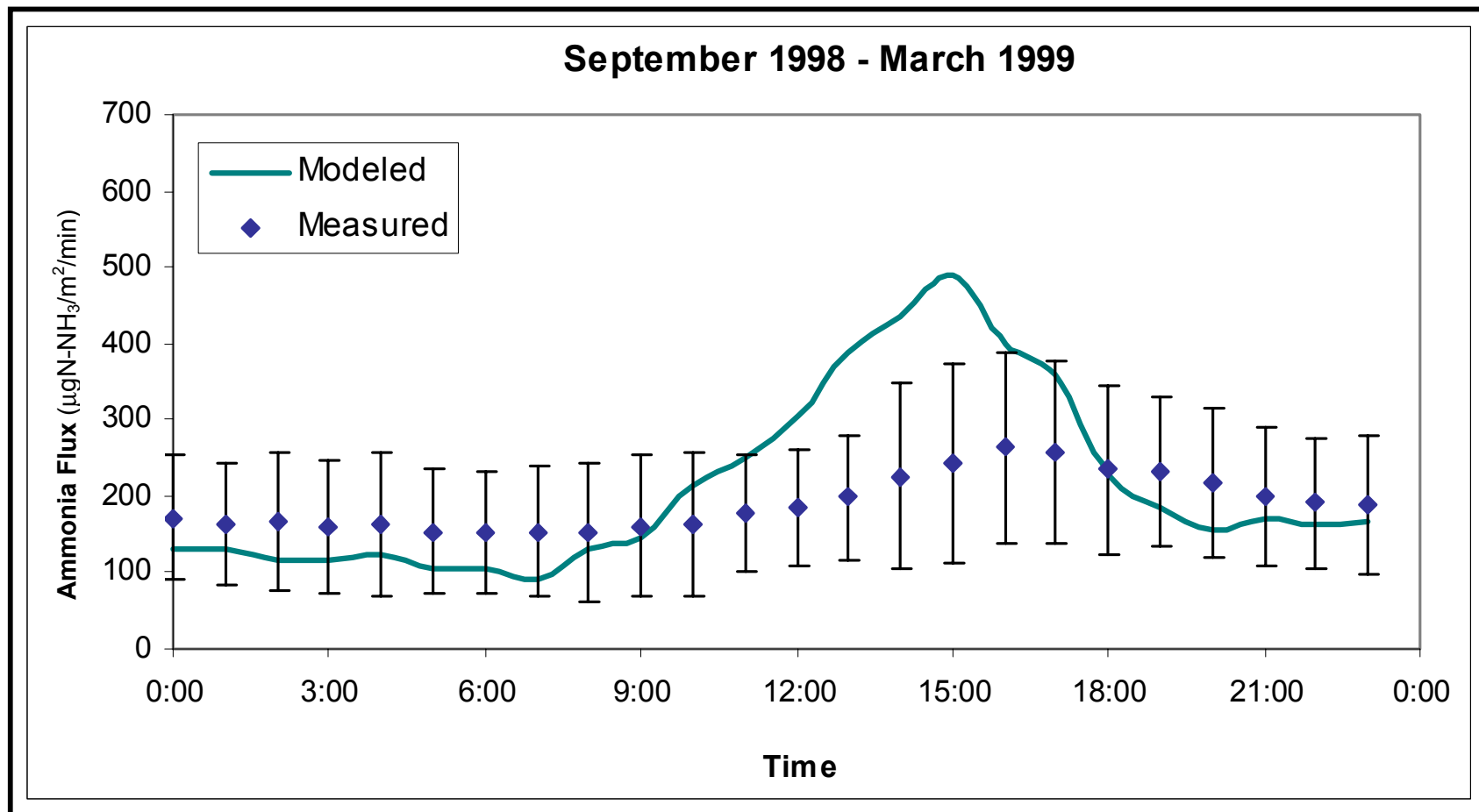


Figure 3.10 Diurnal Comparison of Measured and Modeled Ammonia Flux from September 1998 through March 1999 (Aneja et al., 2001a).

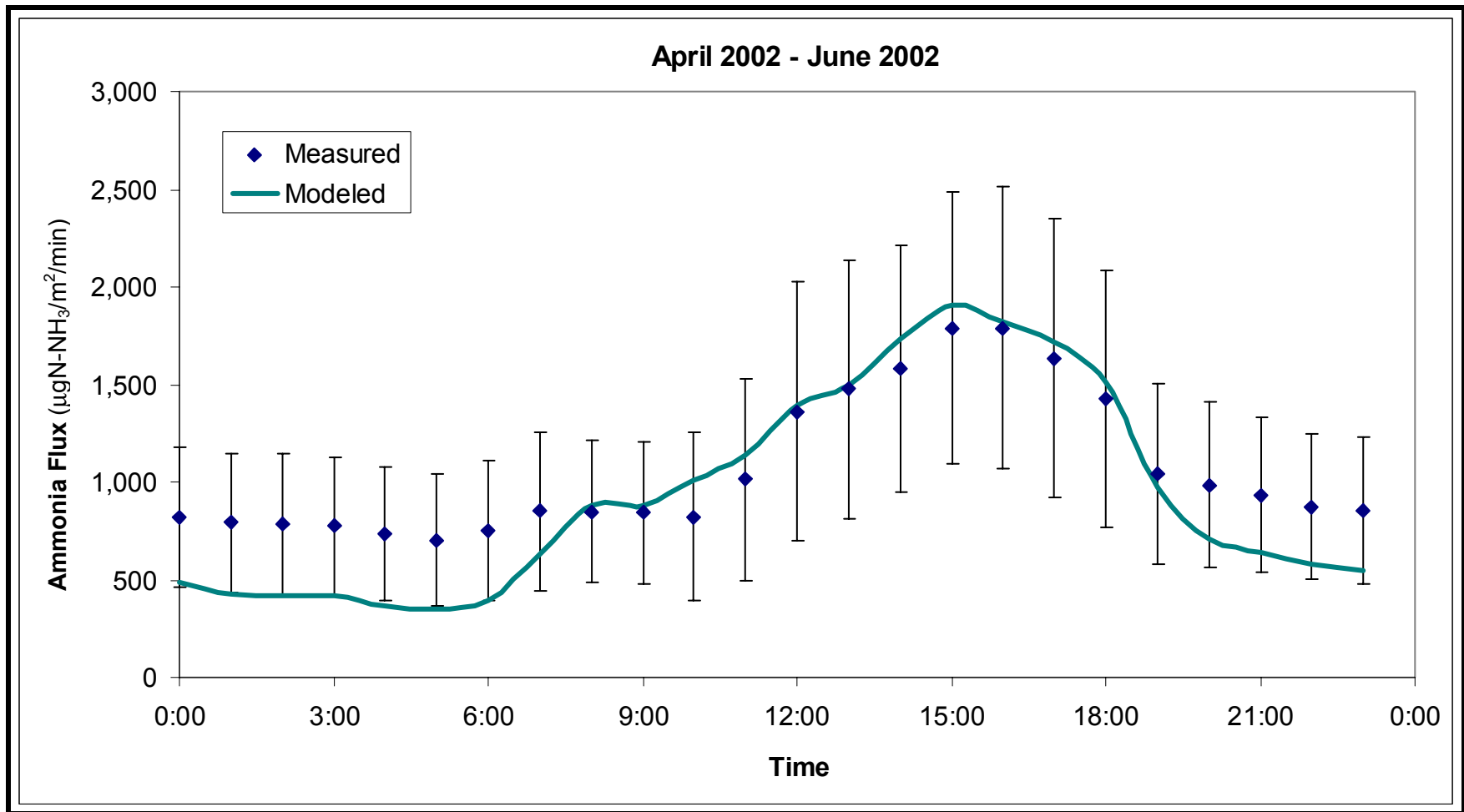


Figure 3.11 Diurnal Comparison of Measured and Modeled Ammonia Flux from April 2002 through June 2002, as part of Program OPEN.

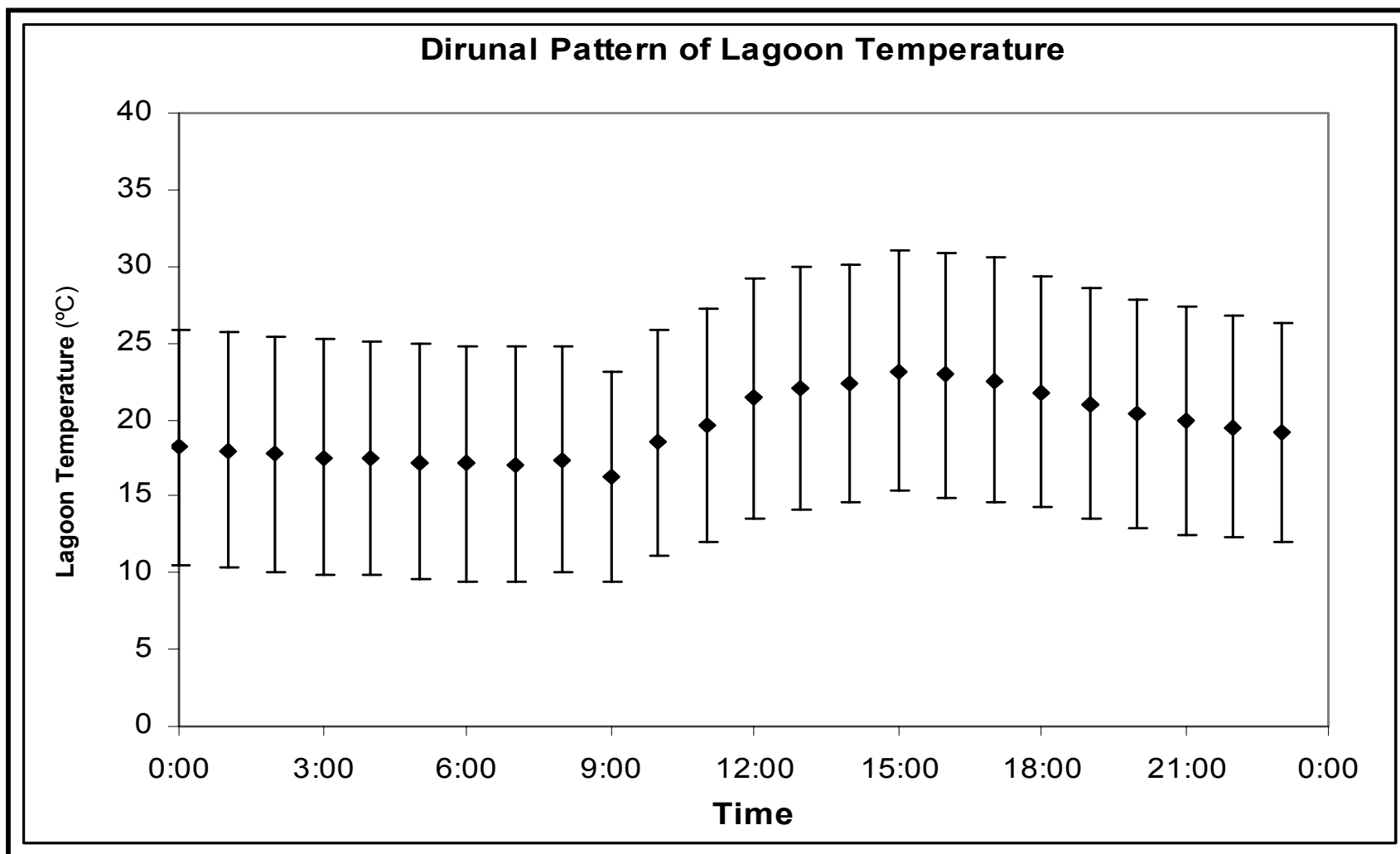


Figure 3.12 Diurnal Pattern of Lagoon Temperature. Each data point represents hourly lagoon temperature averaged over all field campaigns.

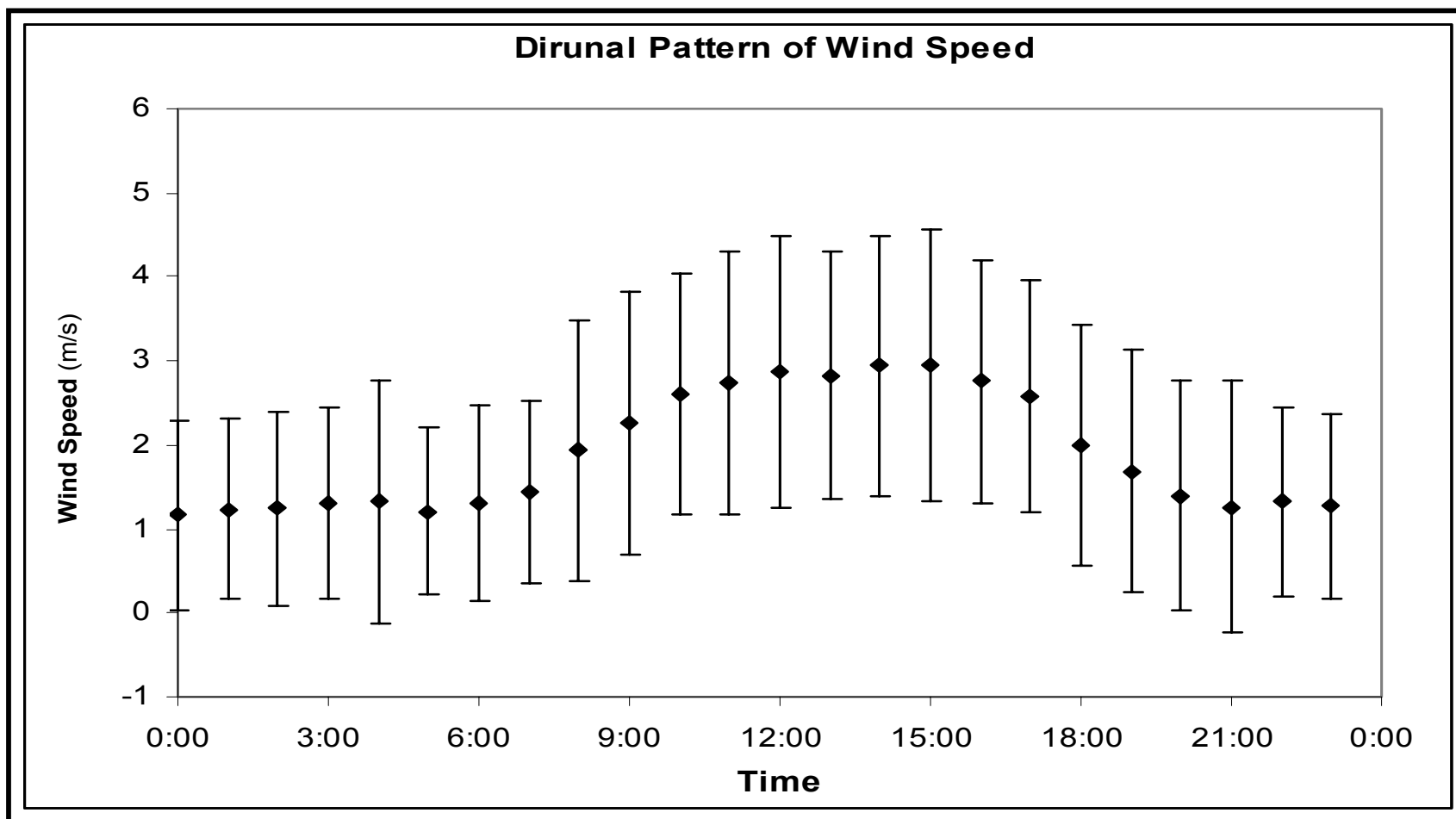


Figure 3.13 Diurnal Pattern of Wind Speed. Each data point represents hourly wind speed averaged over all field campaigns.

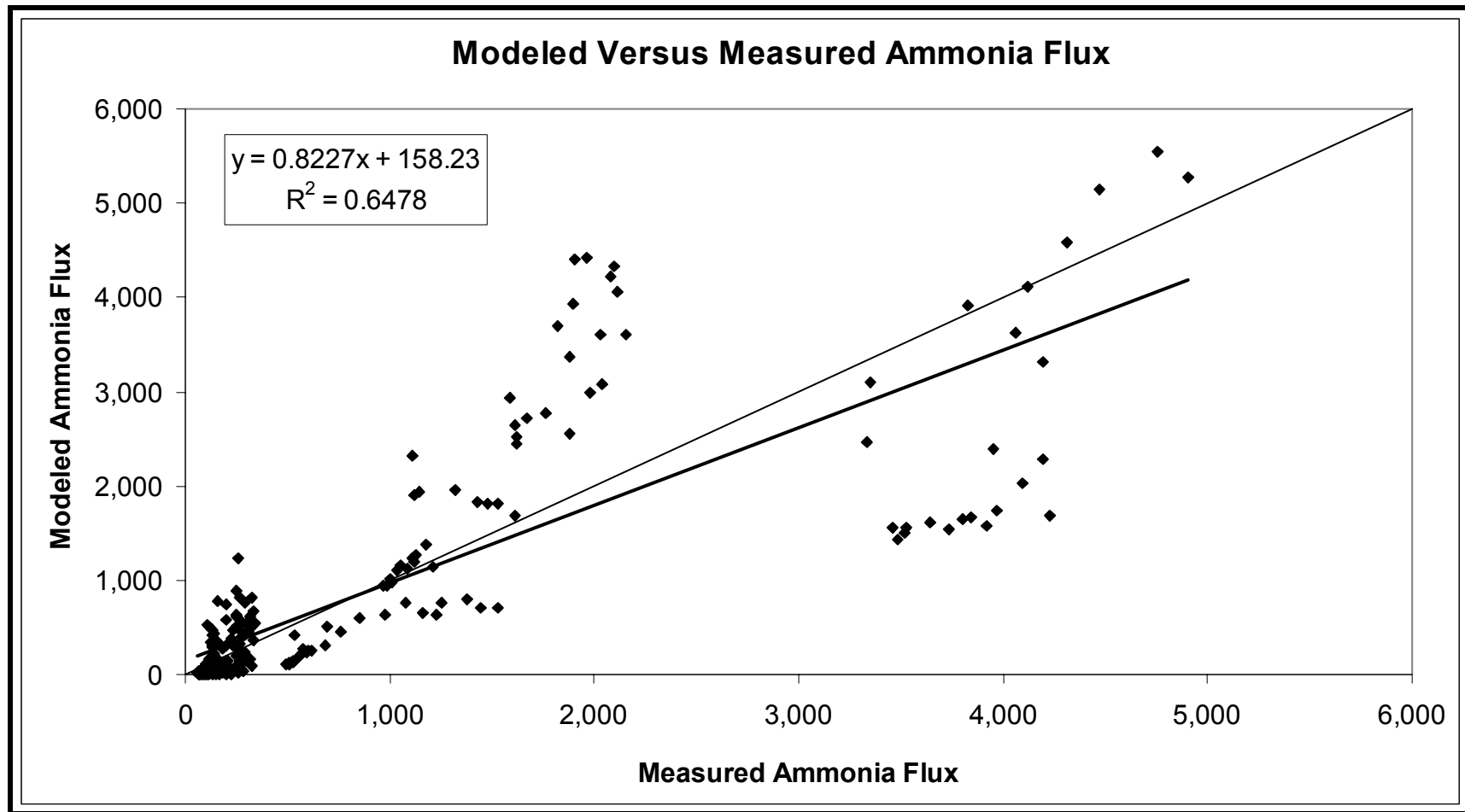


Figure 3.14 Linear Regression of Modeled Flux on Measured Flux. Each data point consists of hourly data averaged over each field campaign. Data from all ten field campaigns are included. Ammonia flux has units of $\mu\text{gN-NH}_3/\text{m}^2/\text{min}$.

CHAPTER IV. CONCLUSIONS AND SUGGESTIONS

Over the past few decades, scientists have become increasingly aware of the effects of atmospheric transport, dispersion and deposition of trace gases. Atmospheric ammonia is a trace gas that has attracted much attention in North Carolina, due to the state's extremely dense population of swine operations in the Coastal Plain Region. In an effort to clearly define the sources of ammonia emissions within North Carolina, the present study analyzes the phenomenon of ammonia flux from commercial swine operations from both an empirical and a theoretical standpoint. Measurements of ammonia flux from both alternative and traditional waste treatment lagoons are presented and compared. Ammonia fluxes from the liquid waste surfaces of the alternative waste treatment technologies have been parameterized by a multivariate physical and chemical model. The ammonia emission factors calculated for three swine operations with alternative waste treatment technologies are consistent with other ammonia emission factors from agricultural operations in North Carolina and abroad. Ammonia flux from other surfaces, including cropland soils, is investigated in order to quantify ammonia emissions from all segments of the commercial swine operations. While the ammonia emissions from cropland soils are smaller in magnitude than those from lagoons, cropland soils may contribute a substantial proportion of the ammonia emissions from an entire swine operation. Further investigation of ammonia emission from soils should occur in order to develop accurate emission factors.

A mechanistic model for ammonia flux across a gas-liquid interface is evaluated with ammonia flux measurements made from waste treatment lagoons using the dynamic flow-through chamber system. Analyzing the process of ammonia flux via both

measurements and modeling triggers improvements in both quantification procedures. By evaluating both the measured and modeled ammonia fluxes with respect to the same set of environmental parameters, discrepancies may be recognized and rectified. Measured and modeled ammonia fluxes both exhibit exponential increases with an increase in lagoon temperature. A linear increase in ammonia flux occurs with an increase in lagoon TAN concentration, as is observed from both field measurements and modeling exercises. Furthermore, a positive correlation between lagoon pH and ammonia flux exists for both measured and modeled ammonia fluxes. The similar responses of measured and modeled ammonia emissions to environmental stimuli indicate that the mechanistic model encompasses fundamental processes that occur within waste treatment lagoons.

Lagoon temperature, lagoon pH, lagoon TAN concentration and wind speed are the dominant input parameters for the coupled model. While the effects of the first three variables on measured and modeled ammonia flux have been well constrained, more investigation into the role of wind speed is necessary. The ammonia flux output by the coupled model clearly increases approximately linearly with wind speed. A clear relation between wind speed and ammonia flux measurements made via the dynamic flow-through chamber system is hard to constrain, for the environment within the chamber is not subject to ambient air flow patterns. However, air flow speed within the chamber has been measured under different combinations of carrier gas flow rate and impeller speeds. The air velocities measured within the chamber fall within the range of measured environmental wind speeds, so they accurately represent the natural environment to some extent, yet they are less variable than environmental wind speeds. A decrease in the

variability of ammonia flux may result, as the mechanistic model would indicate. In order to further define the relationship between inner flow speeds and environmental wind speeds, various carrier gas flow rate and impeller speed regimes should be further explored in the field and in the laboratory. Such experiments would define the effect of wind speed on ammonia flux measurements made with the dynamic chamber system.

Improvements to the field measurement system and the mechanistic model occur continuously, with superior instrumentation and updated theories replacing older versions. Thus, new data should be incorporated into the comparative analysis between measured and modeled ammonia fluxes. The mechanistic model can be further evaluated with a more extensive data set. Such a combination of field measurements and theoretical modeling enhances our ability to accurately quantify ammonia emissions from swine and other agricultural operations.

APPENDIX Validation of a Coupled Mass Transfer with Chemical Reactions Model for Ammonia Flux across a Gas-Liquid Interface

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As the dominant gaseous base specie in the atmosphere, ammonia contributes to various environmental processes, such as aerosol formation, soil acidification, and aquatic eutrophication. Globally, domestic animal waste produces the largest fraction of atmospheric ammonia. Intensive commercial swine operations in the Coastal Plain Region of eastern North Carolina support approximately ten million hogs and release an estimated 250 tons of ammonia per day. The swine operations produce hogs using waste treatment lagoon and spray technology. The coupled mass transfer with chemical reactions model used in this study predicts the flux of ammonia across a waste treatment lagoon-atmosphere interface. The model incorporates the dependence of ammonia flux on lagoon temperature, lagoon pH, wind speed, and the concentration of Total Ammoniacal Nitrogen (TAN) in the lagoon. A comparative analysis between ammonia flux measurements from hog waste treatment lagoons located in central and eastern North Carolina and output from the coupled mass transfer with chemical reactions model indicates that the model output reflects the diurnal pattern of ammonia flux.

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