

ABSTRACT

BAJWA, KANWARDEEP SINGH. Measurements and Modeling of Emissions, Dispersion and Dry Deposition of Ammonia from Swine Facilities. (Under the direction of Dr. Viney P. Aneja and Dr. S. Pal Arya).

Ammonia has recently gained importance for its increasing atmospheric concentrations and its role in the formation of aerosols. Studies have shown increasing atmospheric concentration levels of NH_3 and NH_4^+ , especially in the regions of concentrated animal feeding operations. Atmospheric inputs of reduced nitrogen as ammonia and ammonium by dry and wet deposition may represent a substantial contribution to the acidification of semi natural ecosystems and could also affect sensitive coastal ecosystems and estuaries. The anaerobic lagoon and spray method, commonly used for waste storage and disposal in confined animal feeding operations (CAFO), is a significant source of ammonia emissions. An accurate emission model for ammonia from aqueous surfaces can help in the development of emission factors. Study of dispersion and dry deposition patterns of ammonia downwind of a hog farm will help us to understand how much ammonia gets dry deposited near the farm, and how remaining ammonia gets transported farther away. An experimental and modeling study is conducted of emissions, dispersion and dry deposition of ammonia taking one swine farm as a unit. Measurements of ammonia flux were made at 11 swine facilities in North Carolina using dynamic flow-through chamber system over the anaerobic waste treatment lagoons. Continuous measurements of ammonia flux, meteorological and lagoon parameters were made for 8-10 days at each farm during each of the warm and cold seasons. Ammonia concentrations were continuously measured in the chamber placed over the lagoon using a Thermo Environmental Instrument Incorporated (TECO) Model 17c chemiluminescence ammonia analyzer. A similar ammonia analyzer was used to measure ammonia concentrations at selected locations on the farm. Barn emissions were measured using open-path Fourier transform infrared (OP-FTIR) spectroscopy. A 10 m meteorological tower was erected at each site to measure wind speed and direction, temperature, relative humidity and solar radiation. Data collected from field measurements made at hog waste lagoons in south eastern North Carolina, using the flow

through dynamic chamber technique, were used to evaluate the Coupled Mass Transfer and Chemical Reactions model and Equilibrium model. Sensitivity analysis shows that ammonia flux increases exponentially with lagoon temperature and pH, but a linear increase was observed with an increase in total ammoniacal nitrogen (TAN). Ammonia flux also shows a nonlinear increase with increasing wind speed. Observed ammonia fluxes were generally lower in the cold season than in the warm season when lagoon temperatures are higher. About 41% of the Equilibrium model predictions and 43% of the Coupled model predictions are found to be within a factor of two of the observed fluxes. Several model performance statistics were used to evaluate the performance of the two models against the observed flux data. These indicate that the simpler Equilibrium model does as well as the Coupled model. The possible effects of the “artificial” environment within the chamber, which is different from that in the ambient atmospheric conditions above the open lagoon surface, on the measured fluxes are also recognized. Actual layout of barns and lagoons on the farms was used to simulate dry deposition downwind of the farm. Dry deposition velocity, dispersion and dry deposition of ammonia were studied over different seasons and under different stability conditions. Dry deposition velocities were underpredicted by AERMOD when compared with observed dry deposition velocities. Dry deposition velocities were the highest under near neutral conditions and lowest under stable conditions. The highest deposition at short range occurs under nighttime stable conditions and the lowest deposition occurs during daytime unstable conditions. Significant differences in model predicted depositions over crop and grass surfaces are found under stable conditions. Wind orientation at the farm can also affect deposition of ammonia downwind of the farm.

**MEASUREMENTS AND MODELING OF EMISSIONS, DISPERSION AND DRY
DEPOSITION OF AMMONIA FROM SWINE FACILITIES**

by

KANWARDEEP SINGH BAJWA

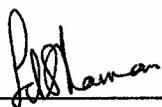
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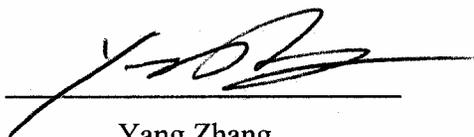
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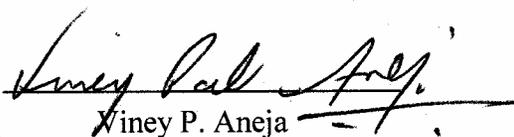
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**Dedicated to
My God
And
My Mother**

BIOGRAPHY

Kanwardeep Singh Bajwa was born on August 12, 1976, in his ancestral village Naserke, Punjab (India) to S. Hardev Singh and Mrs. Sukhwant Kaur. He spent his childhood in his village and did his schooling in Saint Francis Convent School, Fatehgarh Churian, a small town about 11 km from his village. Kanwardeep developed a deep interest in science and mathematics during his high school education. To pursue his interest in science, he joined as undergraduate student at Punjab Agricultural University (PAU) in Ludhiana, India. After completing his undergraduate studies in Agriculture with major in Horticulture, he joined MS in Agricultural Meteorology at Punjab Agricultural University. During his MS, he worked on a project “Wheat yield in relation to Western Disturbance Weather Systems in Punjab”. Kanwardeep was awarded with a merit scholarship for his excellent record in his studies at PAU. He successfully completed his MS in 2001. He also represented and won awards for his college and university as a part of folk dance (Bhangra) team at various national level competitions.

In the fall of 2002, Kanwardeep joined Air Quality Research Group at North Carolina State University to work Dr. Viney P. Aneja and Dr. S. Pal Arya as a doctoral student. While attending NCSU, he worked as a research assistant in the Department of Earth, Marine and Atmospheric Sciences. His doctoral research focused on ammonia emissions and deposition from swine facilities.

During his 3rd year in PhD program, he married his friend of 8 years, Ritu, on January 4, 2005. His wife is presently doing PhD in Ornamental Horticulture from Mississippi State University, Starkville.

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I feel pleasure to sincerely acknowledge co-chairs of my advisory committee, Dr. Viney P. Aneja and Dr. S. Pal Arya, for their patience, guidance and support throughout my doctorate studies. I would also like to thank my committee members Dr. Sethu Raman and Dr. Yang Zhang for their useful inputs during my research. I am very thankful to Dr. Deug-Soo Kim and Air Quality Research Group for all their help and support.

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I would like to thank my family in India and Canada for their love, support and encouragement. Thanks to my niece and nephew Jass and Gary for their love. I am greatly indebted for ever-willing cooperation, help and moral support by my friends here in USA and in India. I want to thank my parents again for all their sacrifices and prayers for my success. I can never repay all they have done for me.

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CHAPTER 1 INTRODUCTION

1.1 Ammonia

Ammonia is an important atmospheric pollutant that plays a key role in several air pollution problems. Ammonia in gaseous form is closely linked to the presence of ammonium in the atmosphere, which in turn acts as neutralizing agent in the atmosphere and also contributes to the regional acidification problems (Warneck, 1999). Ammonium salts remain a major component of inorganic atmospheric aerosols and thus NH_x ($\text{NH}_x = \text{ammonia} + \text{ammonium}$) plays a major role in the physical and chemical processes of the atmospheric nitrogen cycle. Ammonia is gaining increasing importance, as a principle source of atmospheric aerosols (Baek and Aneja, 2004). Ammonia also plays a role in formation of new particles by gas to particle conversion process. Oxidation of SO_2 to H_2SO_4 and its neutralization by ammonia to form sulfate salts is an example of this process (Warneck, 1999).

Earlier, scientists believed that only importance of atmospheric ammonia was its role as source of fixed nitrogen to soil and plants. It was only in mid fifties that Junge (1954, 1956) recognized that ammonia is a single trace gas capable of neutralizing the acids produced by the oxidation of SO_2 and NO_2 in the atmosphere. Ammonia reacts with acidic atmospheric species, such as sulfuric acid, nitric acid and hydrochloric acid, to form ammonium aerosols, e.g., ammonium bisulfate, ammonium sulfate, ammonium nitrate and ammonium chloride. Approximately 10% of the atmospheric NH_3 also reacts with hydroxyl radicals to form amide radicals (Finlayson Pitts and Pitts, 2000; McColloch et al., 1998).

Air mass trajectories suggest that wet and dry 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 ecosystem and estuaries (Walker et al., 2000). Such ecosystems are subject to potential environmental consequences, including aquatic eutrophication and soil acidification. Added nitrogen, regardless of the source, stimulates algae growth in the nitrogen-limited estuaries and shallow coastal waters of North Carolina. The subsequent death and decomposition of these organisms deplete dissolved oxygen in the water (anoxia/hypoxia), a major factor in fish kills. High N-loading can have detrimental effects

in terrestrial ecosystems, effects that can result in the greater export of N to surface and groundwater (Paerl, 1995). Aber et al. (1989, 1998) hypothesized that high N inputs lead to “nitrogen saturation.” Saturation reduces the ability to assimilate and retain further N additions in an ecosystem. The result is an increased nitrate formation and its subsequent loss to surface and groundwater. The level of N input required to saturate an ecosystem will depend to a very large extent on the makeup of the community and will include many non-biotic factors related to the properties of the soil and climate. Ammonia can cause foliar injury to exposed plants, reduce growth and productivity, increase soil acidity and decrease biodiversity. In agricultural systems, addition of NO_3^- to soil (initially as NH_3 or NH_4^+) and the consequent increases in emissions of N_2O (nitrous oxide, a greenhouse gas) and leaching of NO_3^- to the ground and the surface waters are of major environmental concern (Krupa, 2003). North Carolina’s Albemarle-Pamlico Sound system is one of many North American, European and Asian estuarine and coastal ecosystems impacted by atmospheric nitrogen deposition which are exhibiting advance signs of eutrofication in form of recurring toxic and non-toxic phytoplankton blooms (Pearl, 1991, 1995; Paerl et al., 1993).

1.1.1 Ammonia Emissions

With the increasing human demand for food production, the use of nitrogen containing fertilizers and production of domestic livestock is increasing. Domestic animal waste is the major source of ammonia emissions. Estimates of global ammonia emissions 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, 1999).

As a regional-scale example, in an emission inventory prepared by the European Environment Agency, covering 28 European countries, over 92% of the more than 5.6 million metric tons of ammonia emitted was agricultural in origin. Of this 92%, about 80% was associated with the decomposition of livestock manure and the rest with the volatilization of fertilizer-N (NCDENR, 1999).

Ammonia is increasing in importance in the rural atmosphere over the eastern United States (Aneja et al, 2001a, 2000). The number of commercial swine facilities in North Carolina has increased dramatically, with the state's hog population increasing from approximately 2.8 million in 1990 to 9.8 million in 1997 when a moratorium on new hog farms was placed (Figure 1.1). Much of the increase in hog industry has occurred in coastal plane region, where more than 8.5 million hogs currently reside (Aneja et al., 2000) (Figure 1.2).

Measurements made at National Atmospheric Deposition Program and National Trends Networks sites in North Carolina show an increasing trend in the ammonium concentration in the precipitation since 1990 (Walker et al., 2000). This trend occurs in conjunction with an increase in the number of nearby swine operations. Coincident with the growth of swine numbers in the state, there has been a decline in the total number of farms raising swine (NCDENR, 1999) (Figure 1.1). The decrease in the total number of farms raising swine is the result of the closure and consolidation of small family farms and a move toward the industry preference of large farms that house more than 2,000 heads. The confined method of feeding and waste removal currently being used by the swine industry creates substantial quantities of anaerobic waste.

For reduction strategies to put in place, we need to know the total budget of ammonia and contribution of various sources. Such a task requires extensive field measurements and modeling. Table 1.2 gives us nitrogen emission inventory for North Carolina. Swine farms contribute to about 20% of nitrogen emissions. The major source of nitrogen from swine farms is ammonia. Different approaches have been made to quantify the ammonia emission sources.

Livestock waste emission estimates used by EPA are based on emission factors recommended in a 1994 study by Battye et al. (1994), which are derived from European measurements, where animal practices may vary significantly from United States. Each emission factor includes total emissions resulting from animal housing, grazing, manure storage, and land spreading. Battye et al. (2003) estimated new inventory and compared with EPA and NCDENR estimates for ammonia emissions from North Carolina. It shows that livestock waste contributes from 80 to 89% of ammonia emissions in North Carolina. Any uncertainty in this source can lead to big differences in estimated emissions. Lower

and upper range of emissions vary from 100000 to 180000 Mg/year ($\text{Mg} = 10^6\text{g}$), which indicates a large uncertainty in ammonia emission estimates. Major uncertainties in emission estimates seem to be related to the use of simple emission factors, many of which are highly empirical or have been derived from measurements carried out under conditions which deviate considerably from those following modern practices of handling and applying manure and fertilizers (Schjorring, 1998).

Seventy five percent of swine production systems in North America and northern Europe use anaerobic or liquid/ slurry systems for waste holding, which is a major source of ammonia emissions (Safley et al., 1992). Emission rates from waste lagoons are difficult to measure, requiring specialized equipment and appropriate transport-measurement technology to obtain realistic emissions in relation to variable climatic and management conditions where animal production occurs. An emission model to predict ammonia emissions would reduce the expense of determining emissions on the large number of lagoons.

Measurements of ammonia flux from hog waste treatment lagoons (Aneja et al., 2001b; Aneja et al., 2000) and from fertilized and unfertilized soils (Roelle, 2001) have recently been made and analyzed with respect to corresponding environmental parameters, including lagoon and soil temperature, pH and total ammoniacal nitrogen (TAN).

Studies have also been done to model ammonia emissions. Previous studies have utilized theoretical models to study ammonia emissions from animal waste and soil. Koelliker and Minor (1973) developed a desorption model for ammonia emissions using two film theory. The overall mass transfer co-efficient (Halsem et al, 1924) in this model depends on wind velocity and temperature, and gives an emission of zero under calm conditions with no wind.

Asman et al. (1998a) reviewed the ammonia research, including process description and emission factors for ammonia emissions. Olsen and Sommer (1993) modeled ammonia emissions from stored slurry considering effects of wind speed and surface cover. A model to predict ammonia volatilization from flooded soils using TAN, pH, temperature, floodwater depth and wind speed was developed by Jayaweera and Mikkelsen (1990). Another investigation to predict ammonia volatilization from manure

pits in swine buildings was done by Zhang et al. (1994). De Visscher et al. (2002) developed a two-layer model to study emissions from anaerobic lagoon. The model uses effluent concentration, water temperature, wind speed and effluent pH. It takes into account the aqueous equilibrium reaction of ammonia and ammonium, the adsorption of ammonium on the suspended organic material, and the diffusive transfer of ammonia and ammonium across liquid and air boundary layers.

Aneja et al. (2001b) developed a Coupled mass transfer and chemical reactions model and an Equilibrium model to simulate ammonia emissions from swine waste lagoons. Their two-layer models are based on the two-film theory using molecular transfer of ammonia across the lagoon-air interface. The Coupled mass transfer and chemical reactions model also takes into account pseudo-first order reaction of ammonia with water and acidic species (H_2SO_4 , HNO_3 , HCl) in the atmosphere. It incorporates air temperature, lagoon temperature, pH, wind speed, TAN and ambient ammonia concentration. This model shows exponential increase with lagoon temperature and pH and linear increase with wind speed and TAN.

This study will include comparison of measured ammonia emission fluxes from swine waste treatment lagoon systems and modeled ammonia emission fluxes using the models developed by Aneja et al. (2001). Comparison of measured and modeled emission fluxes will help us to validate the models and also help us to make improvements in them and in measuring techniques of required parameters in this model.

1.1.2 Ammonia Deposition

Gaseous ammonia undergoes dry deposition, with deposition velocities ranging up to 14 cm/s (Hanson and Lindberg, 1991; Phillips et al., 2004). Due to its high deposition velocity and its reactivity in the atmosphere, gaseous ammonia has a relatively short atmosphere lifetime, on the order of a few days or less (Warneck, 1999). Ammonium aerosols deposit more slowly than gaseous ammonia, with deposition velocity of roughly 0.2 cm/s (Warneck, 1999). 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.

NH₃ emissions from source region, primarily evolving from swine and poultry operations, are found to increase NH₄⁺ concentration in precipitation at locations up to ~ 80 km away (Walker et al., 2000). Poor et al., (2001) studied nitrogen deposition in Tampa Bay area. They found that 46% of nitrogen deposition occurs by dry deposition, of which NH₃ was a major contributor. Phillips (2003) showed that NH₃ contributed 47% of the total nitrogen dry deposited in the Neuse river watershed. NH₃ contributes to roughly half of the total nitrogen deposition in Denmark, according to a study conducted by Howmand et al. (1993, 1994).

Results presented in NCDENR (1999) report demonstrate that ammonia emissions from swine production facilities can significantly enhance dry deposition of NH₄⁺-N to adjacent forest canopies. At the Eastern Farm site, NH₄⁺-N dry deposition was approximately two times (10.2 kg N/ha) that from wet deposition during the collection period of August 6, 1997 to April 16, 1998. Total NH₄⁺-N deposition to the forest floor (from both wet and dry deposition) was 14.5 kg N/ha. The dry deposition of NH₄⁺-N observed at the Eastern Farm site also enhanced the apparent dry deposition of chloride (Cl⁻) (9.2 kg Cl⁻/ha) and sulfate (SO₄²⁻) (17.1 kg SO₄/ha).

Adverse effects on sensitive ecosystems caused by high N deposition can be reduced by lowering the emissions and, to a limited extent, also by removing sources close to the ecosystem to be protected (Asman et al., 1998b). This study has been selected to help develop an ammonia emission model from waste treatment lagoon that can be used to develop ammonia emission factors to study the transport of ammonia and its dry deposition downwind of the swine facilities taking one swine unit as a study model. We will also study dispersion and dry deposition of ammonia downwind of swine facilities, to quantify ammonia concentrations downwind. As NH₃ dry deposition velocity shows a diurnal and seasonal variation (Phillips et al., 2004), we will study diurnal variation of ammonia along with seasonal variations.

1.2 Methods and Materials

1.2.1 Dynamic Flow-Through Chamber system

A flow through dynamic chamber system with a variable-speed continuous impeller or stirrer (Aneja et al., 2000; Chauhan, 1999; Kim et al., 1994; Kaplan et al.,

1988) was used to determine NH_3 flux from lagoon surfaces (Figure 1.3). A translucent plastic cylindrical chamber of height 45.7 cm and diameter 25 cm (volume of 24.34 liter) was used. It was fitted in a circular hole cut in the center of a floating platform of 1.2 m \times 1.2 m. The cylinder is fitted into the hole in the center of the platform, so that it penetrates into the lagoon surface by ~ 7 cm. The chamber was lined with a 5 mm thick fluorinated ethylene propylene (FEP) Teflon sheet throughout the inside surface of the chamber. Variable speed motor driven Teflon stirrer or impeller was used to mix the air inside the chamber. A carrier gas of compressed air travels into the chamber through a $\frac{1}{4}$ inch Teflon at a variable flow rate of 4-8 litre per minute (lpm) set by mass flow controller and monitored by a datalogger. The sample from the chamber travels through another $\frac{1}{4}$ inch Teflon tubing to the detection instrument. Teflon tubing and lining was used to minimize the chemical reaction with the sample stream. With the flow rate of 5 lpm, this equates to sample residence time of approximately 5 minutes in the system and 3 seconds in the lines at steady state. The vent in the sample line prevents the system from over pressurizing and was bubble tested periodically.

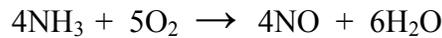
Air inside the chamber is well mixed with impeller speeds 40-60 rpm for this study. Roelle (1996) found that varying the speed of Teflon propeller within the above range did not produce any significant changes in the calculated NO soil flux using the chamber method. Johansson and Granat (1984) measured the pressure differences between outside atmosphere and air inside a chamber using a tilted water manometer. They found that pressure differences were below detection limits (0.2 mm H_2O). Bunton (1999) conducted an experiment to explore possible differences between air temperature inside the chamber and ambient temperature. His study found maximum temperature differences of 2.5 $^{\circ}\text{C}$ and 3.4 $^{\circ}\text{C}$ over two 24-hr experiments, which may have a minimal effect on the temperature of the lagoon water inside the chamber. Sample from chamber passes through Teflon tubing (6.35 mm outside diameter, 3.97 mm inside diameter) to the ammonia detection instruments. This whole system is lined with Teflon or stainless steel fitting in order to minimize chemical reactions with sample flow.

1.2.2 Temperature Controlled Mobile Laboratory

The mobile laboratory used in our field measurements consists of a modified Ford Aerostar van with 13,500 BTU air conditioner unit. All the instrumentations are placed in this van. The temperature inside the van is regulated for effective performance of the ammonia analyzers. A 110 volt outlet was used to power the air conditioning and all detection instruments.

1.2.3 NH₃ Detection Instrumentation

Thermo Environmental Instrument Incorporated (TECO) Model 17c chemiluminescence ammonia analyzers were continuously used to monitor ammonia concentrations during ammonia flux measurement periods. Theory of working of this instrument relies on high temperature catalytic conversion of NH₃ to NO,



and subsequent detection of NO based on the reaction between ozone and nitric oxide.



The photon produced in this reaction is detected by the photomultiplier tube converted into concentration of NO after calibration with known standards (TECO, 1999).

The sample stream entering analyzer is divided into 3 paths. The first path mixes the sample with ozone (O₃), and all of the nitric oxide (NO) in the sample reacts with ozone and give us nitrogen dioxide (NO₂) concentration. Second path passes through a molybdenum converter (325 °C) which converts all oxidized forms of nitrogen to nitric oxide. This sample then reacts with ozone to quantify the concentration of all oxides of nitrogen. Third sample line passes through stainless steel converter (750 °C) which converts all nitrogen oxides and ammonia into nitric oxide, which gives total nitrogen (N_T). The sample stream alternates between three flow paths. Total ammonia is calculated by the difference between total nitrogen and total oxides of nitrogen as

$$[\text{NH}_3] = [\text{N}_T] - [\text{NO}_x] \quad (1)$$

Ammonia analyzers are placed in the mobile laboratory. These work most effectively within a certain range of temperatures. Air conditioner in mobile lab helps to keep

temperature within that range. Further details of the TECO Model 17C ammonia analyzer and its calibration procedure are given by Philips et al. (2003).

1.2.4 Meteorological Measurements

A 10 m meteorological tower was erected at each site to measure wind speed and direction, temperature, relative humidity and solar radiation. A Met One Instruments Model 034B-L Windset was used to measure wind speed and direction at 10 m above the surface. This model consists of an integrated cup anemometer and wind vane. Accuracy of measured horizontal wind speed is ± 0.12 m/s for wind speeds below 10.1 m/s and $\pm 1.1\%$ of reading for wind speed above 10.1 m/s. The horizontal wind direction has an accuracy of $\pm 4^\circ$ and a threshold of 0.4 m/s. Air temperature and relative humidity (RH) measurements were made at a height of 2m facing north with a model HMP45C temperature and relative humidity probe housed in a radiation shield. RH accuracy is $\pm 2\%$ (0-90% RH) and $\pm 3\%$ (90-100% RH) while air temperature accuracy is 0.2 – 0.5 °C. Solar radiation measurements were also made at the 2m height but facing south using a model LI200X Silicon Pyranometer probe. Solar radiation has an absolute error in natural daylight of 5% maximum and 3% typical. (CSI Operator Manual Reference)

1.2.5 Ambient Ammonia and Lagoon Parameters

Ambient ammonia concentration was measured at 10 m height, using a filter with 1 μm pores prevent the aerosols and dust particles to get in the instrument. Teflon tubes were used to carry the sample to the ammonia analyzer. CSI Model 11-L50 Innovative sensors pH probe continuously monitored lagoon pH during lagoon NH_3 emission measurement periods. Two C107 temperature probes measured lagoon temperature simultaneously inside the chamber and 0.5 m outside the chamber. Difference in lagoon temperatures inside and outside the chamber were found to be insignificant (less than 1 °C). These pH and temperature probes were submerged in the lagoon at the depth of 15-20 cm. Lagoon water samples were collected daily from measurement sites and submitted to the Department of Biological and Agricultural Engineering (BAE), North Carolina State University, for analysis of TAN measurements.

1.2.6 Lagoon Sampling Scheme

Flux chamber was moved everyday in a random manner over the lagoon surface and Instruments were spanned everyday and flux chamber was flushed every time when it was moved to other part of the lagoon, to prevent the build up of ammonia in the chamber. Sampling locations were within 3m from the lagoon berm for easy access to the chamber without using a boat.

1.2.7 Automated Data Acquisition System

A Gateway laptop computer and a Campbell Scientific CR23X Datalogger (PC208W software) were used continuously collect data from all the instruments. It was placed in mobile laboratory. It stored data for ammonia from lagoon, lagoon temperature, lagoon pH, meteorological parameters and ambient ammonia. Data stored was averaged over 15 minutes. Data from datalogger was downloaded daily on laptop.

1.2.8 Ammonia Flux Calculation

The mass balance equation to calculate ammonia flux for the dynamic chamber system (Kaplan et al., 1988) is,

$$\frac{dC}{dt} = \left(\frac{q[C_{air}]}{V} + \frac{JA}{V} \right) - \left(\frac{LA_w}{V} + \frac{q}{V} \right) [C] - R \quad (2)$$

- C NH₃ concentration in a chamber (ppbv)
- C_{air} NH₃ concentration in ambient air (ppbv)
- q Flow rate of compressed air through the chamber (lpm)
- V Volume of chamber (24.34 liter)
- A Surface area covered by chamber (m²)
- A_w Inner surface area of the inner and upper wall surface of the chamber (0.374 and 0.209 m² respectively)

- L Total loss of ammonia in the chamber per unit area (m min^{-1}) due to reaction with inner and upper walls of the chamber
- h Internal height of the chamber
- J Emission flux per unit area ($\mu\text{g NH}_3\text{-N m}^{-2} \text{s}^{-1}$)
- R Rate of change due to reactions in gas phase

Zero air was used as a carrier gas, so that C_{air} is assumed to be zero. Since the chamber is assumed to be well mixed, concentration, C , is constant within the chamber. At steady state conditions, the change of concentration with respect to time will be zero. Also, since zero gas is used as a carrier gas, R is zero. With these conditions/assumptions, Eq (2) is simplified as:

$$\frac{J}{h} = \left(\frac{LA_w}{V} + \frac{q}{V} \right) C_{eq} \quad (3)$$

Loss term L was determined experimentally while equilibrium-state ammonia (C_{eq}), flow rate (q) and dimensions of the chamber (V and h) were all measured. Kaplan et al. (1988) devised a method for calculating the loss term by determining the slope of the best-fitted line through a plot of

$$- \ln \left[\frac{C_{eq} - C(t)}{C_{eq} - C_o} \right]$$

versus time (t). For this experiment, C_o is the initial equilibrium state NH_3 concentration measured by the chamber system at a constant flow rate of 12-14 lpm, C_{eq} is the measured NH_3 concentration at a second equilibrium state reached at a reduced flow rate of 4-6 lpm into the chamber system, at $C(t)$ denotes the NH_3 concentration at any time, t , during the transition between the first and second equilibrium states. Then the loss term L is determined as

$$L = \left(slope - \frac{q}{V} \right) \left(\frac{V}{A_w} \right)$$

where A_w represents the area of the inner walls of the chamber.

1.2.9 Sampling sites

Ammonia flux measurements were made at swine facilities in south eastern North Carolina under the OPEN (Odor, Pathogens and Emissions of Nitrogen) project. Two of these sites employed Lagoon and Spray technology (LST) and others used potential Environmentally Superior Technologies (ESTs). At all the sites, measurements were made during two, two-week long periods, representing warm and cold seasons, respectively. The 2 LST farms and 9 EST farms used in this study are listed in Table 1.3 and are briefly described below. Their locations and measurement periods are given in Table 1.3.

Description of sites: (Table 1.3)

Stokes Farm is located near Trenton, NC, in Pitt County. Waste from the hog barns were flushed periodically (4 times a day) with recycled lagoon water and discharged into a storage pond from a single effluent pipe.

Moore Farm is located near Kinston, NC, in Jones County. Waste from all the hog barns was flushed out with recycled lagoon water and discharged into a storage pond from eight effluent pipes, one for each hog barn.

Brown's of Carolina # 93 (EKOKAN) is located near Bladenboro, NC, in Bladen County. Biofilters are used to separate the solids from waste before it was pumped in lagoon.

Corbett # 1, 3, 4 (BEST: Solids separation/gasification for energy and ash recovery centralized system) are located near Rose Hill, NC, in Duplin County.

Corbett # 2 (Recip) is located near Rose Hill, NC, in Duplin county. This technology employs wetland cells or basins in which alternating anaerobic and aerobic conditions are created to remove nitrogen from the waste stream.

Howard farm (Constructed wetland system) is located in Onslow county. This project involves the utilization of constructed wetlands for effluent treatment following primary screening and solids separation.

Barham farm (In-Ground Ambient Temperature Anaerobic Digester System) is located near Clayton NC, in Johnston county. The ambient digester consists of an impermeable cover over an in-ground digester. Methane gas produced in this digester is used for electricity production at the site.

Harrell's farm is located near Harrells, NC, in Sampson county. The permeable cover used is the Bio-Cap ML, designed to reduce ammonia emissions and odor.

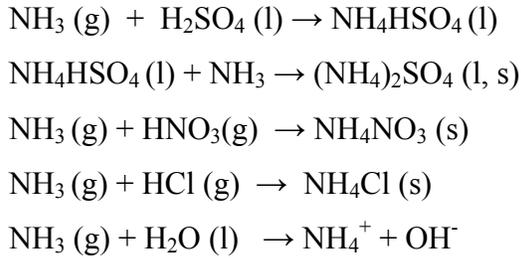
Hunt farm is located near Wilson NC, in Edgecombe county. Pulverizer Air Dryer (PAD) technology is to be used to separate the solid and liquid portions of the waste stream from swine farms and dry the solid portion.

Carroll's farm is located near Warsaw NC, in Duplin county. Waste flows first to what is described as a covered anaerobic pond; however, the cover is a layer of aerated water sprayed over the top of the pond. This aerated layer is designed to reduce ammonia emissions and odor. Wastewater then flows to an aerated nitrification pond and finally to a denitfication/irrigation storage pond.

Vestal farm is located near Kenansville NC, in Duplin county. This farm employs a mesophilic digester as well as aeration and a wastewater filtering and disinfection systems.

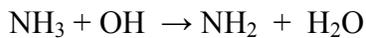
1.3 Model Description

The process of the conversion of ammonia in the atmosphere is a complex one involving various reactions, whose direction and rate are determined by atmospheric factors like relative humidity, pH and temperature etc. Most of the gaseous ammonia (~90%, Aneja et al., 1997) in the troposphere is converted into NH_4^+ aerosols by reaction of ammonia with sulfuric acid and hydrochloric acid. The following gas(g), liquid(l) and solid (s). phase reactions summarize NH_4^+ aerosol production (Finlayson-Pitts and Pitts, 1986),



Ammonium aerosols return to the ground by dry and wet deposition processes. Tropospheric life of ammonia is less than 5 days, so it is removed in the region of its source itself (~80 km). Walker (1998) suggested that in North Carolina, the source may impact the distances of approximately 80 km depending on the wind direction.

Additional losses (~10%, Aneja et al., 1997) of ammonia are attributable to reactions of ammonia with hydroxyl radical (lifetime ~ 165 days, Warneck, 1988):



1.3.1 Two-film theory

The principle characteristic of this two-film transport model (Figure 1.4) is an air-liquid interface for the exchange between water and air (Whitman, 1923, Cussler 1996). The interface between the two phases is a boundary between the two fluid layers. Each layer is a laminar surface layer of thickness t_i (for liquid phase $t_i = t_L$ and for air $t_i = t_a$) extending from air-liquid interface and to a well-mixed (turbulent) region in the interior of the lagoon and atmosphere, respectively. All the resistance to mass transfer across the interface is due to the layer in which transport is by molecular processes.

Reaction rate for the chemical reaction in the liquid and gas phase, in general, will depend on the local concentration of the gas, any other reactant with which it reacts, and other physical factors such as temperature and pH. The background concentrations of reactants in chemical processes in the liquid and gas phase involving ammonia do not have significant variations. The ammonia concentrations C_L and C_a at the other boundary of the films have been assumed to be constant. There are also uncertainties in the values of the rate constants determined by various researchers. The overall effect on flux due to variation in the rate parameters will be assumed insignificant and constant values for reaction rate constants have been determined (Malik, 1999).

1.3.2 Simplified Diffusion Equation

Considering an element of differential thickness dz in the vertical direction with the unit cross sectional area, diffusion equation can be simplified as

$$D_i \left(\frac{d^2 C}{dz^2} \right) = k_{ri} \times [C] \quad (4)$$

where C is ammonia concentration, k_{ri} is the reaction constant in the phase i , $D_i = D_L$ and $k_{ri} = k_{rl}$ for liquid and $D_i = D_a$ and $k_{ri} = k_{ra}$ for air, respectively. This equation follows directly from the basic advection equation, given by Arya (1999), after the assumption of steady state and horizontal homogeneity of flow and concentration fields are made.

1.3.3 Solution of Basic Diffusion Equation

Eq. 4 is a differential equation of second order whose general solution is (Malik, 1999),

$$C_{(z)} = Ae^{r \times z} + Be^{-r \times z} \quad (5)$$

where, $r = \sqrt{\frac{k_{ri}}{D_i}}$ and subscript i can be read as L for liquid and a for air.

Boundary Conditions:

LIQUID PHASE

$$\begin{aligned} z = 0; C_L(0) &= C_L \\ z = t_L; C_L(t_L) &= C_{Li} \end{aligned} \quad (6)$$

GAS PHASE

$$\begin{aligned} z = 0; C_a(0) &= C_{ai} \\ z = t_a; C_a(t_a) &= C_a \end{aligned} \quad (7)$$

SOLUTION IN LIQUID PHASE;

Applying the boundary conditions in liquid phase, one can determine A and B in Eq. 5 as

$$A = \frac{C_{Li} - C_L e^{-r_L t_L}}{e^{r_L t_L} - e^{-r_L t_L}} \quad (8)$$

$$B = \frac{C_L e^{r_L t_L} - C_{Li}}{e^{r_L t_L} - e^{-r_L t_L}} \quad (9)$$

Substituting for A and B in Eq. (5), one obtains

$$C_{(z)} = \frac{C_{Li} (e^{r_L z} - e^{-r_L z}) - C_L (e^{(z-t_L)r_L} - e^{-(z-t_L)r_L})}{e^{r_L t_L} - e^{-r_L t_L}} \quad \text{for } 0 < z \leq t_L \quad (10)$$

Where $r_L = (k_{rL}/D_L)^{1/2}$, k_{rL} is the overall reaction rate constant for reactions of ammonia in the liquid, and D_L is the diffusivity of ammonia in liquid phase.

SOLUTION IN THE GAS PHASE

Similarly equation can be solved for gas phase and solution to eq. (5) with boundary conditions in gas phase are as follows,

$$C_{(z)} = \frac{C_a (e^{r_a z} - e^{-r_a z}) - C_{ai} (e^{(z-t_a)r_a} - e^{-(z-t_a)r_a})}{e^{r_a t_a} - e^{-r_a t_a}} \quad \text{for } 0 < z \leq t_a \quad (11)$$

where $r_a = (k_{ra}/D_a)^{1/2}$

k_{ra} is an overall rate constant for ammonia reactions in gas phase (s^{-1}), and

D_a is diffusivity of ammonia in the air (cm^2/sec).

C_{ai} and C_{Li} are related by the henry's law constant as,

$$C_{ai} = H C_{Li} \quad (12)$$

Another boundary condition to solve the above equations is that fluxes at interface are equal

$$\begin{aligned} J &= -D_L (dC/dz) && \text{at } z = t_L, \text{ in liquid phase} \\ &= -D_a (dC/dz) && \text{at } z = 0, \text{ in gas phase} \end{aligned} \quad (13)$$

This leads to the following expression for C_{Li} ,

$$C_{Li} = \frac{2D_a \times C_a \times r_a \times (e^{r_L t_L} - e^{-r_L t_L}) + 2D_L \times C_L \times r_L \times (e^{r_a t_a} - e^{-r_a t_a})}{HD_a \times r_a (e^{r_a t_a} + e^{-r_a t_a})(e^{r_L t} - e^{-r_L t_L}) + D_L \times r_L (e^{r_a t_a} - e^{-r_a t_a})(e^{r_L t} + e^{-r_L t_L})} \quad (14)$$

1.3.4 Ammonia Flux

Ammonia flux J is the diffusion flux at top of the air film and it is determined by the following relationship at the interface of the air film and turbulent region,

$$J = -D_a (dC/dz) \text{ at } z = t_a \quad (15)$$

Using equation (11) with $z = t_a$ and $C_{ai} = HC_{Li}$, one obtains the following expression for the vertical ammonia flux:

$$J = D_a \times r_a \left(\frac{C_a (e^{r_a t_a} + e^{-r_a t_a}) - 2H \times C_{Li}}{e^{r_a t_a} - e^{-r_a t_a}} \right) \quad (16)$$

1.3.5 Ammonia Flux with no Reactions (Equilibrium Model)

Equation (16) is an expression of flux considering chemical reactions of ammonia in the liquid and air films. If we consider negligible chemical reactions in the liquid and air films, this expression should reduce to the form of equilibrium equation,

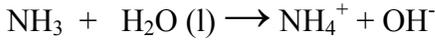
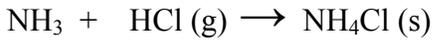
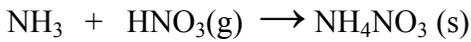
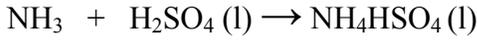
$$J = -K(C_a - HC_L) \quad (17)$$

where $K = 1/(H/k_L + 1/k_a)$, is the overall mass transfer coefficient (m/s).

where k_L and k_a are the mass transfer coefficients (m/s) for ammonia in liquid and air respectively and H is the Henry's law coefficient. Equation (17) is the equilibrium transport equation for the flux.

1.3.6 Ammonia Flux with Reactions (Coupled mass transfer and chemical reactions model)

In order to determine the coupled transport and chemical reaction ammonia flux, we have considered ammonia's reversible reactions in the solution and forward reactions only in the atmosphere. We can therefore determine the overall reaction rate for reactions of the ammonia in the atmosphere as follows,



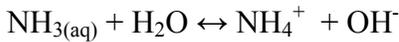
Above equation leads to the following relationship,

$$d[\text{NH}_3]/dt = (k_{\text{H}_2\text{SO}_4} [\text{H}_2\text{SO}_4] + k_{\text{HNO}_3} [\text{HNO}_3] + k_{\text{HCl}} [\text{HCl}] + k_{\text{OH}} [\text{OH}^-]) * [\text{NH}_3]$$

and the reaction rate,

$$k_{\text{ra}} = k_{\text{H}_2\text{SO}_4} [\text{H}_2\text{SO}_4] + k_{\text{HNO}_3} [\text{HNO}_3] + k_{\text{HCl}} [\text{HCl}] + k_{\text{OH}} [\text{OH}^-] \quad (18)$$

However since ammonia's reaction in the liquid phase is reversible, the overall reaction rate will depend on the direction of the reaction. Olander (1960) has given the equations for predicting the effect of various types of equilibrium chemical reactions considering simultaneous mass transfer and equilibrium chemical reactions. Ammonia's reaction in the solution is as below,



Solution for C_{Li} is obtained as,

$$C_{\text{Li}} = \frac{\frac{2D_a C_a r_a}{e^{r_a t_a} - e^{-r_a t_a}} + C_L \times \frac{D_L}{t_L} \times \left(1 + \frac{D_{\text{NH}_4}}{D_L} \times \frac{K_L}{[\text{OH}^-]}\right)}{\text{HD}_a r_a \times \left(\frac{e^{r_a t_a} + e^{-r_a t_a}}{e^{r_a t_a} - e^{-r_a t_a}}\right) + \frac{D_L}{t_L} \times \left(1 + \frac{D_{\text{NH}_4}}{D_L} \times \frac{K_L}{[\text{OH}^-]}\right)} \quad (19)$$

Equation 19 gives the value of C_{Li} which is substituted into equation 16 to calculate the ammonia flux values.

1.3.7 Mass Transfer Coefficients

Halsam et al. (1924), Mackey and Yeon (1983), and Ibusuki and Aneja (1984), have determined the mass transfer coefficients. Mass transfer equations by Halsam et al. (1924) gives zero flux values at wind speed of zero. Mackey and Yeon (1983) used 11 hydrocarbon compounds of varying Henry's law constant. They have empirically correlated the mass transfer coefficients in terms of friction velocity and Schmidt number. The empirical values of the mass transfer coefficients in air and water arrived by Mackey and Yeon are given below,

Mass transfer coefficient (in m/s) for the air,

$$k_a = 1 \times 10^{-3} + 46.2 \times 10^{-3} U^* Sc_a^{-2/3} \quad (20)$$

where U^* is friction velocity in m/s.

Mass transfer coefficient (in m/s) for the water,

$$k_L = 1 \times 10^{-6} + 34.1 \times 10^{-4} U^* Sc_L^{-1/2} \quad (\text{for } U^* > 0.3) \quad (21)$$

$$k_L = 1 \times 10^{-6} + 144 * 10^{-4} U^{*2.2} Sc_L^{-1/2} \quad (\text{for } U^* < 0.3) \quad (22)$$

Schmidt number (Sc_a and Sc_L) is the ratio of diffusion coefficient of ammonia to kinetic viscosity for respective medium (air or water). These mass transfer coefficients provide more realistic estimates at zero wind speed, which is not the case with other studies.

Another approach to calculate mass transfer coefficients is the mechanistic approach (Schwartz, 1986). Advantage of mechanistic approach is that we do not need to empirically derive equations for mass transfer coefficients. Limitation in empirical approach is that error in calculation of dimensionless numbers could lead to uncertainty in flux calculation. Schwartz gave the formula to calculate the diffusion from the bulk liquid (droplet) to surrounding atmosphere based on the sum of diffusion resistances across the liquid and gas film. Schwartz's equation is conceptually similar to equations we used for our model. But it represents overall mass transfer coefficient and not the individual mass transfer coefficients as we need for our emission model. It also has its own limitations. Schwartz (1986) mentions that potential problem is to determine film Thickness. Gas boundary film thickness can be determined from Sherwood number, which is further calculated using Reynolds and Schmidt number. Aqueous film thickness

of 0.01 R and 0.01 R (R= radius of droplet) are used for fast and slow aqueous kinetics reaction rates of the gas species. We have used Mackey and Yeon (1983) mass transfer coefficients for calculations in the equilibrium model.

1.3.8 Temperature Dependence

Density of ammonia in water and air are dependent on temperature of aqueous solution and air. Density and dynamic viscosity of water and air are related to the temperature of water and air respectively as per relationship provided by CRC 1989-90. Kinetic viscosity is the dynamic viscosity divided by the density. Diffusivity of water and air were used from Cussler (1996) as follows,

$$D_w = \frac{D_{25} \times (273 + T_L) \times \mu_T}{298 \times \mu_{25}} \quad (23)$$

where,

D_w and D_{25} are diffusivity at lagoon temperature and 25 °C, respectively.

μ_T and μ_{25} are dynamic viscosity at lagoon temperature and 25 °C, respectively.

$$D_a = \frac{1 \times 10^{-3} \times (273 + T_a)^{1.75} \times \sqrt{\left(\frac{1}{m_1} + \frac{1}{m_2}\right)}}{p \times \left\{ \left(\sum V_{i1}\right)^{\frac{1}{3}} + \left(\sum V_{i2}\right)^{\frac{1}{3}} \right\}^2} \quad (24)$$

where,

m_1 = molecular weight of ammonia = 17g

m_2 = molecular weight of air = 29g

P = 1 atmosphere

V_{11} = diffusion volume of ammonia = 14.9 (at 1 atm)

V_{12} = diffusion volume of air = 20.1 (at atm)

Henry's law coefficient for flux equation is adopted from Hales and Drewes (1979) and related with lagoon temperature with the following relations,

$$\text{Log } H = -1.69 + 1477.7/T_L \quad (25)$$

1.4 AERMOD – Dispersion model

AERMOD (AERMIC Dispersion Model) model is designed to support the EPA's regulatory modeling programs to study short range dispersion and dry deposition. It was developed to replace ISC3 (Industrial Source Complex) dispersion model.

AERMOD is a steady-state plume model (USEPA, 1998). In the stable boundary layer (SBL), it assumes the concentration distribution in a continuous source plume to be Gaussian in both the vertical and horizontal. In the convective boundary layer (CBL), the horizontal distribution on the plume is also assumed to be Gaussian, but the vertical distribution is described with a bi-Gaussian probability density function (pdf). Additionally, in the CBL, AERMOD treats “plume lofting,” whereby a portion of plume mass, released from a buoyant source, rises to and remains near the top of the boundary layer before becoming mixed into the CBL. AERMOD also tracks any plume mass that penetrates into the elevated stable layer, and then allows it to re-enter the boundary layer when and if appropriate. For sources in both the CBL and the SBL AERMOD treats the enhancement of lateral dispersion resulting from plume meander.

Using a relatively simple approach, AERMOD incorporates current concepts about flow and dispersion in complex terrain. Where appropriate the plume is modeled as either impacting and/or following the terrain. This approach has been designed to be physically realistic and simple to implement while avoiding the need to distinguish among simple, intermediate and complex terrain, as required by other regulatory models. As a result, AERMOD removes the need for defining complex terrain regimes. All terrain is handled in a consistent and continuous manner while considering the dividing streamline concept in stably stratified conditions.

AERMOD characterizes the PBL through both surface and mixed layer scaling. It constructs vertical profiles of required meteorological variables based on measurements and extrapolations of those measurements using similarity (scaling) relationships. Vertical profiles of wind speed, wind direction, turbulence, temperature, and temperature gradient are estimated using all available meteorological observations. AERMOD is designed to run with a minimum of observed meteorological parameters. As a replacement for the ISC3 model, AERMOD can operate using data of a type that is readily available from National Weather Service (NWS) stations. AERMOD requires

only a single surface measurement of wind speed (measured between $7 z_o$ and 100 m, where z_o is the surface roughness height), wind direction and ambient temperature. Like ISC3, AERMOD also needs observed cloud cover. However, if cloud cover is not available (e.g., from an on-site monitoring program) two vertical measurements of temperature (typically at 2 and 10 meters), and a measurement of solar radiation can be substituted. A full morning upper air sounding is required in order to calculate the convective mixing height throughout the day. Surface characteristics (surface roughness, Bowen ratio, and albedo) are also needed in order to construct similarity profiles of the relevant PBL parameters. AERMOD accounts for the vertical inhomogeneity of the PBL in its dispersion calculations. This is accomplished by "averaging" the parameters of the actual PBL into "effective" parameters of an equivalent homogeneous PBL.

Figure 1.5 shows the flow and processing of information in AERMOD. The modeling system consists of one main program (AERMOD) and two pre-processors, AERMET (AERMOD Meteorological Preprocessor) and AERMAP (AERMOD Terrain Preprocessor). The major purpose of AERMET is to calculate boundary layer parameters for use by AERMOD. The meteorological INTERFACE, internal to AERMOD, uses these parameters to generate profiles of the needed meteorological variables. In addition, AERMET passes all meteorological observations to AERMOD.

The AERMET is the meteorological preprocessor for the AERMOD. Input data can come from hourly cloud cover observations, surface meteorological observations and morning upper air soundings. Output includes surface meteorological observations and parameters and vertical profiles of several atmospheric parameters. AERMET is designed to be run as a three-stage process (Figure 1.6) and operate on three types of data -- National Weather Service (NWS) hourly surface observations, NWS twice-daily upper air soundings, and data collected from an on-site measurement program such as from an instrumented tower. The first stage extracts (retrieves) data and assesses data quality. The second stage combines (merges) the available data for 24-hour periods and writes these data to an intermediate file. The third and final stage reads the merged data file and develops the necessary boundary layer parameters for dispersion calculations by AERMOD. AERMET then calculates the PBL parameters: friction velocity (u^*), Obukhov length (L), convective velocity scale (w^*), temperature scale (θ^*), mixing height

(z_i), and surface heat flux (H). These parameters are then passed on to the INTERFACE (which is within AERMOD) where similarity expressions (in conjunction with measurements) are used to calculate vertical profiles of wind speed (u), lateral and vertical turbulent fluctuations (F_v , F_w), potential temperature gradient ($d\theta/dz$), and potential temperature (θ).

The AERMAP is a terrain preprocessor designed to simplify and standardize the input of terrain data for the AERMOD. Input data include receptor terrain elevation data. The terrain data may be in the form of digital terrain data that is available from the U.S. Geological Survey. Output includes, for each receptor, location and height scale, which are elevations used for the computation of air flow around hills. In present study, we assumed flat rural terrain. So AERMAP will not be used in this study.

The model is capable of handling multiple sources, including point, volume, and area source types. Line sources may also be modeled as a string of volume sources or as elongated area sources. Several source groups may be specified in a single run, with the source contributions combined for each group. Source emission rates can be treated as constant throughout the modeling period, or may be varied by month, season, hour-of-day, or other optional periods of variation. These variable emission rate factors may be specified for a single source or for a group of sources.

The AERMOD model has considerable flexibility in the specification of receptor locations. The user has the capability of specifying multiple receptor networks in a single run. The user can input elevated receptor heights in order to model the effects of terrain above (or below) stack base, and may also specify receptor elevations above ground level to model flagpole receptors. There is no distinction in AERMOD between elevated terrain below release height and terrain above release height, as with earlier regulatory models that distinguished between simple terrain and complex terrain. For applications involving elevated terrain, the user must also input a hill height scale along with the receptor elevation.

AERMOD includes dry deposition algorithms to calculate dry deposition of given gas. The dry deposition flux, F_d , is calculated as the product of the concentration, χ_d , and a deposition velocity, V_d , computed at a reference height, z_r :

$$F_d = C \times V_d \quad (26)$$

where

F_d = dry deposition flux ($\mu\text{g}/\text{m}^2/\text{s}$),

C = concentration ($\mu\text{g}/\text{m}^3$), calculated at reference height, z_r ,

V_d = deposition velocity (m/s)

The dry deposition flux is calculated on an hourly basis, and summed to obtain the total flux for the user-specified period. The default output units for dry deposition flux in AERMOD are g/m^2 . Deposition velocity of gases is calculated as

$$V_d = 1/(R_a + R_b + R_c) \quad (27)$$

where

R_a = Aerodynamic resistance (s/m)

R_b = Quasilaminar resistance for bulk surface (s/m)

R_c = Bulk surface resistance (s/m)

1.5 Objectives

The primary objectives of this research initiative are:

- 1) Measurement of ammonia flux from swine waste treatment lagoons from facilities in South Eastern North Carolina using flux chamber system.
- 2) Validate the coupled mass transfer and chemical reaction model using the ammonia flux measurements from swine waste treatment lagoons.
- 3) To study the downwind short range dispersion of ammonia using US EPA's regulatory short range dispersion model, AERMOD, with respect to different times of the day, meteorological conditions and season.
- 4) To study dry deposition of ammonia downwind of swine facilities using AERMOD, with respect to different times of the day, meteorological conditions and season.

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Table 1.1 Estimates of sources and sinks of ammonia (Tg year^{-1} as nitrogen).
 (1Tg= 10^{12} g)

Process	Warneck (1988)	Schlesinger and Hartley (1992)
Sources		
Coal combustion	≤ 2	2
Automobiles	0.2	0.2
Biomass burning	2-8	5
Domestic animals	22	32
Wild animals	4	-
Human excrements	3	4
Soil/plant emissions	15	10
Fertilizer losses	3	9
Oceans	-	13
Sum of sources	54	75
Sinks		
Wet deposition	38	46
Dry deposition	10	10
Reaction with OH	1	1
Sum of sinks	49	57

Table 1.2. Nitrogen emission inventory for North Carolina (NCDENR, 1999).

<i>Source</i>	<i>Nitrogen Species Emitted</i>	<i>Estimated Tons of Nitrogen Emitted per Year¹</i>	<i>% of Total N²</i>
Highway Mobile (1990)	NO _x	78,509	23.31
Point Sources (1994)	NO _x	77,798	23.10
Area & Non-Road Mobile (1990)	NO _x	24,452	7.26
Biogenic NO _x	NO _x	9,926	2.95
Swine (1995)	NH ₃	68,540	20.35
Cattle (1995)	NH ₃	24,952	7.41
Broilers (1995)	NH ₃	13,669	4.06
Turkeys (1995)	NH ₃	16,486	4.89
Fertilizer Application (1995)	NH ₃	8,270	2.46
“Other” Chickens (1995)	NH ₃	6,476	1.92
Industrial NH ₃ Point Sources (1995)	NH ₃	1,665	0.49
Human (1995) ³	NH ₃	1,629	0.48
Publicly Owned Treatment Works (1995) ⁴	NH ₃	4,440	1.32
Total		336,812	100

1: NO_x emissions are reported as if all emissions were NO₂ although most emissions occur as NO, and convert to NO₂ in the atmosphere (NO_x in the atmosphere is about 95% NO₂). Calculation of nitrogen emitted per year from NO_x sources is from multiplying tons of NO_x per year by (14/46). Calculation of nitrogen emitted per year from ammonia sources is from multiplying tons of ammonia per year by 14/17.

2: About 56.6% of nitrogen is from NO_x and about 43.4% is from NH₃.

3,4: Emission factors are based on limited data and are not believed as accurate as for other sources.

Table 1.3. List of Swine farms and measurement periods.

Farm	Latitude	Longitude	Warm season	Cold season
Moore's farm (Jones county)	35.14°N	77.47°W	May 12-23, 2003 and Jul 28 – Aug 8, 2003	Sept 30 - Oct 11, 2002 and Jan 27 – Feb 7, 2003
Stokes farm (Pitt county)	35.43°N	77.48°W	Sept 9-20, 2002	Jan 6-17, 2003
Howard farm (Onslow county)	34.84°N	77.50°W	Jun 2-14, 2002	Dec 2-13, 2002
Barham farm (Johnston county)	35.70°N	78.32°W	Apr 1-12, 2002	Nov 11-22, 2002
Corbett # 2 (Duplin county)	34.84°N	77.96°W	Jun 2-13, 2003	Mar 10-21, 2003
Corbett # 1,3,4 (Duplin county)	34.84°N	77.96°W	Sept 8-19, 2003, Sept 29- Oct 3, 2003	Dec 1-16, 2003
BOC 93 (Bladen county)	34.49°N	78.78°W	Jun 16 - 27, 2003	Mar 31- Apr 11 2003
Harrell's farm (Sampson county)	34.75°N	78.23°W	May 31 – Jun 11, 2004	Jan 26 – Feb 6, 2004
Hunt farm (Edgecombe county)	35.78°N	77.74°W	Apr 19-30, 2004	Feb 16-27, 2004
Vestal farm (Duplin county)	34.94°N	77.94°W	Aug 2 – Aug 13, 2004	Mar 8-19, 2004
Carroll's farm (Duplin county)	34.04°N	78.03°W	Jun 21-Jul 2, 2004	Mar 29 – Apr 9, 2004

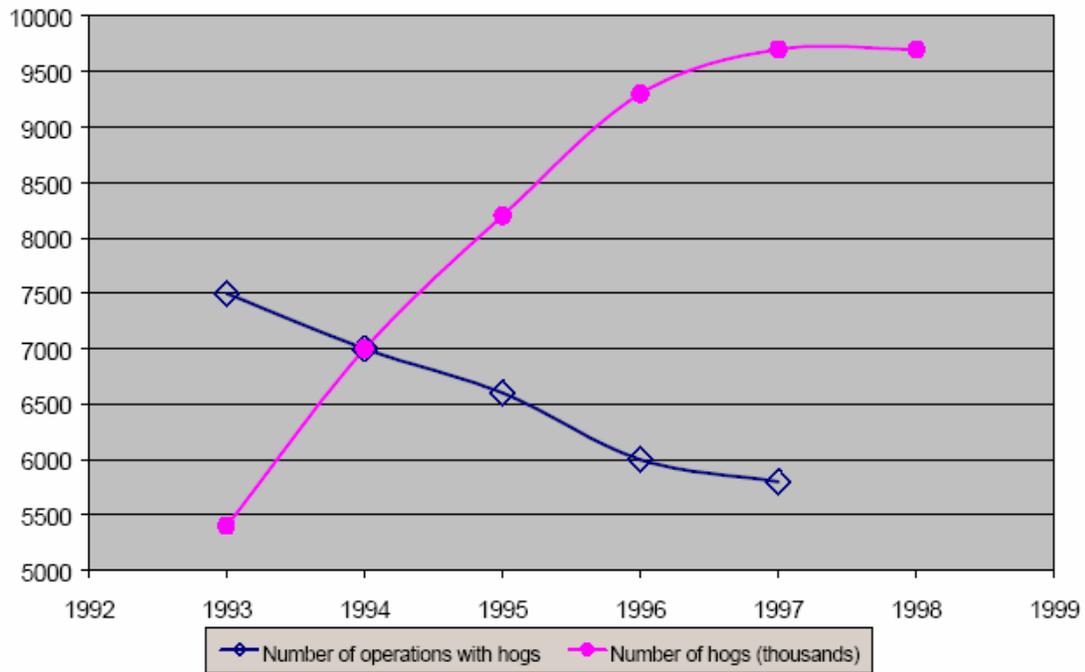


Figure 1.1. Hog population and number of farms in North Carolina. (Source NCDENR, 1999).

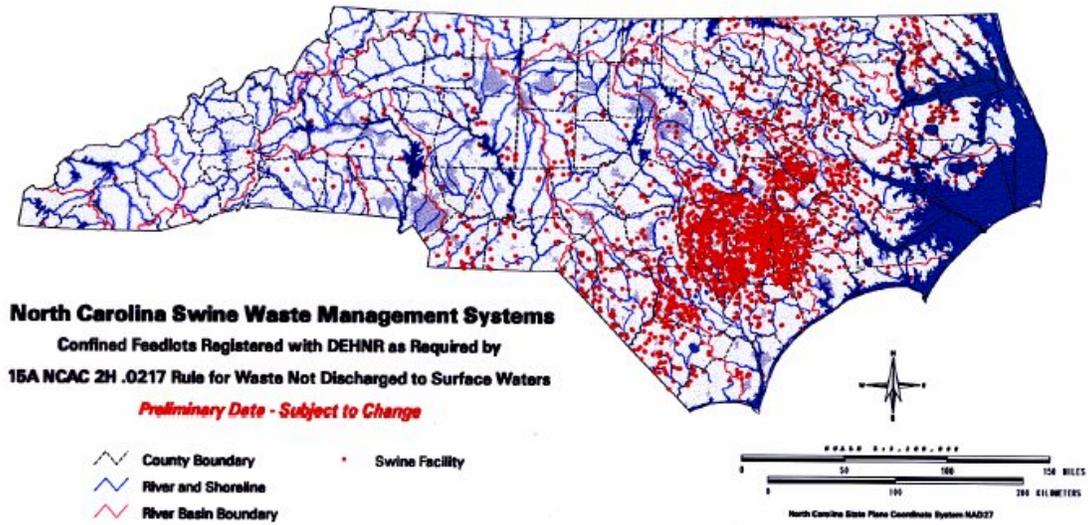


Figure 1.2. Swine distribution in North Carolina (Source Aneja et al., 2000)

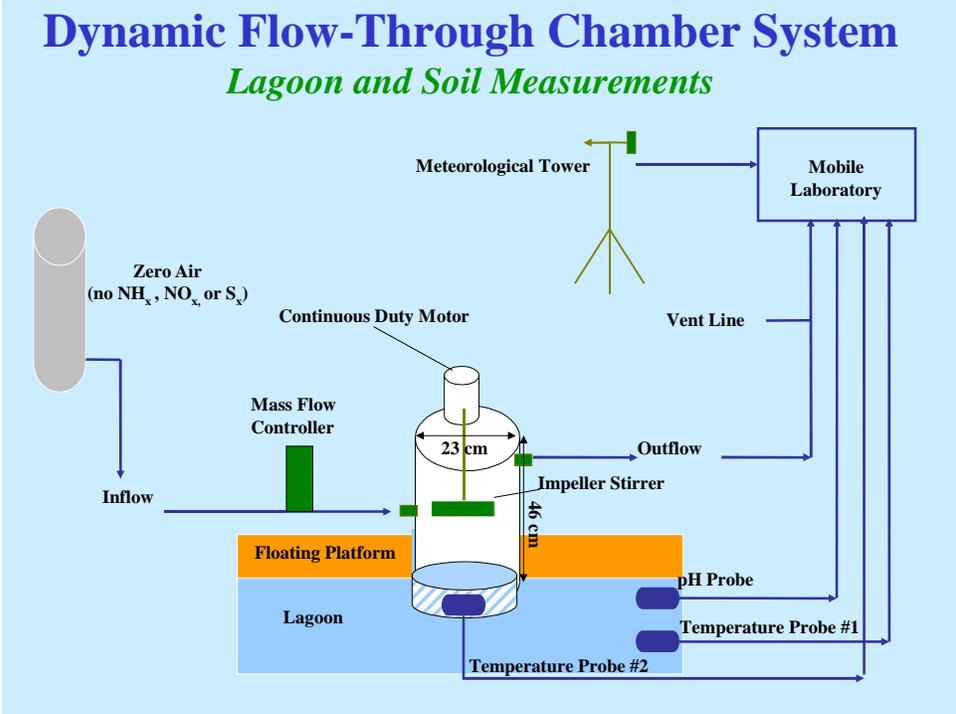


Figure 1.3 Ammonia Flux measurement Dynamic Flow Through Chamber System.

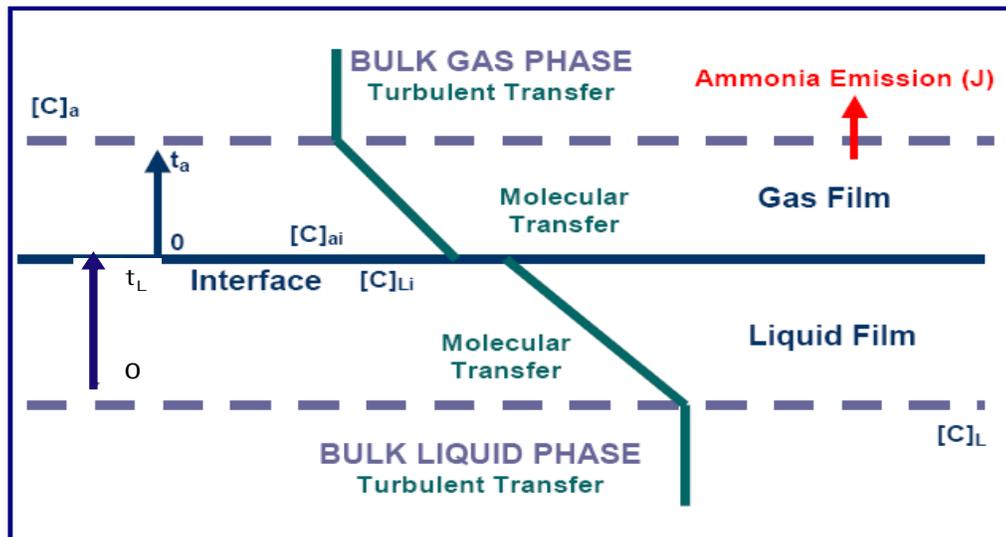


Figure 1.4. Two film theory of mass transfer (Aneja et al., 2001b)

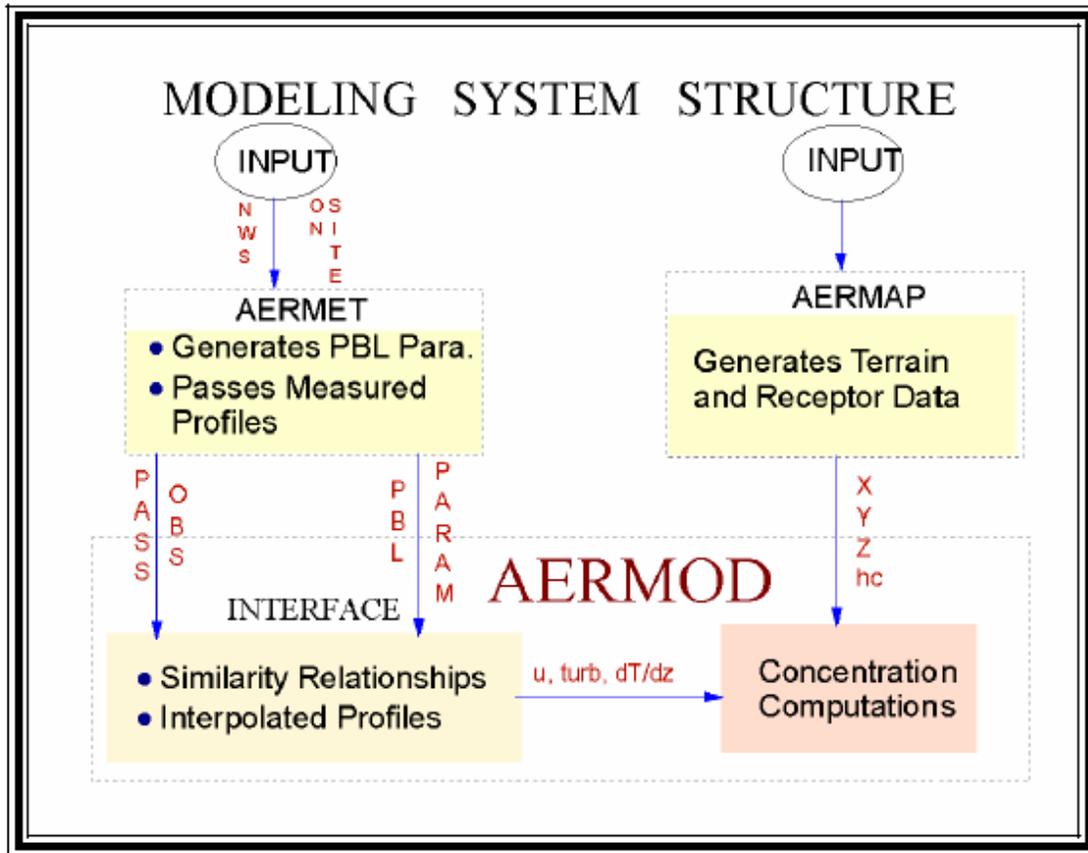


Figure 1.5. Data flow in the AERMOD modeling system (USEPA, 1998).

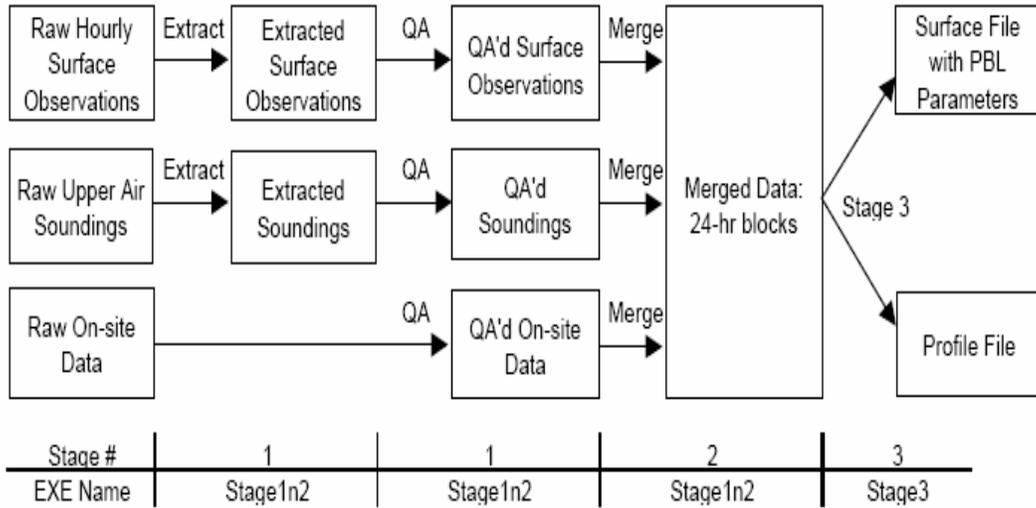


Figure 1.6. AERMET Processing (USEPA, 1998).

CHAPTER II Measurement and Estimation of Ammonia Emissions From Lagoon- Atmosphere Interface using a Coupled Mass Transfer and Chemical Reactions Model, and an Equilibrium Model

Abstract

Ammonia has recently gained importance for its increasing atmospheric concentrations and its role in the formation of aerosols. The anaerobic lagoon and spray method, commonly used for waste storage and disposal in confined animal feeding operations (CAFO), is a significant source of ammonia emissions. An accurate emission model for ammonia from aqueous surfaces can help in the development of emission factors. Data collected from field measurements made at hog waste lagoons in south eastern North Carolina, using the flow through dynamic chamber technique, were used to evaluate the Coupled Mass Transfer and Chemical Reactions model and Equilibrium model developed by Aneja et al., (2001a). Sensitivity analysis shows that ammonia flux increases exponentially with lagoon temperature and pH, but a linear increase was observed with an increase in total ammoniacal nitrogen (TAN). Ammonia flux also shows a nonlinear increase with increasing wind speed. Observed ammonia fluxes were generally lower in the cold season than in the warm season when lagoon temperatures are higher. About 41% of the Equilibrium model predictions and 43% of the Coupled model predictions are found to be within a factor of two of the observed fluxes. Several model performance statistics were used to evaluate the performance of the two models against the observed flux data. These indicate that the simpler Equilibrium model does as well as the Coupled model. The possible effects of the “artificial” environment within the chamber, which is different from that in the ambient atmospheric conditions above the open lagoon surface, on the measured fluxes are also recognized.

2.1 Introduction

Ammonia is an important atmospheric pollutant that plays a key role in several air pollution problems. Ammonia in the gaseous form is closely linked to the presence of ammonium in the atmosphere, which in turn acts as a neutralizing agent in the atmosphere and also contributes to the regional acidification problem (Warneck, 1999). Ammonium salts remain a major component of inorganic atmospheric aerosols and thus NH_x ($\text{NH}_x = \text{ammonia} + \text{ammonium}$) plays a major role in the physical and chemical processes of the atmospheric nitrogen cycle. Ammonia is gaining increasing importance as a principle source of atmospheric aerosols (Baek et al, 2004). Ammonia reacts with acidic atmospheric species, such as sulfuric acid, nitric acid and hydrochloric acid, to form ammonium aerosols namely ammonium bisulfate, ammonium sulfate, ammonium nitrate and ammonium chloride. Approximately 10% of the atmospheric NH_3 also reacts with hydroxyl radicals to form amide radicals (Finlayson-Pitts and Pitts 2000; McColloch et al 1998).

Ammonia concentrations increased in the rural atmosphere over eastern North Carolina between 1982 and 1997 (Aneja et al., 2001b). The number of commercial swine facilities in North Carolina has increased dramatically, with the state's hog population increasing from approximately 2.8 million in 1990 to 9.8 million in 1996 when a moratorium on new commercial hog farms was placed (NCDENR, 1999). Measurements made at National Atmospheric Deposition Program/National Trends Networks sites in south eastern North Carolina showed an increasing trend in the ammonium concentration in the precipitation from 1990 to 1997 (Walker et al., 2000). As a regional-scale example, an emission inventory prepared by the European Environment Agency, covering 28 European countries, shows that over 92% of the more than 5.6 million metric tons of ammonia emitted was agricultural in origin. Of this ammonia, about 80% was associated with the decomposition of livestock manure and the rest with the volatilization of fertilizer-N (NCDENR, 1999). Seventy five percent of swine production systems in North America and northern Europe use anaerobic or liquid/slurry systems for waste holding, which are major sources of ammonia emissions (Safley et al., 1992).

Measurements of ammonia emissions from hog waste treatment lagoons (Aneja et al., 2001a; Aneja et al., 2000) and from fertilized and unfertilized soils (Roelle , 2001)

have been made and analyzed with respect to relevant environmental parameters, including lagoon or soil temperature, pH and TAN (Total Ammoniacal Nitrogen). Harper et al. (2004) studied the ammonia emissions from hog lagoons using micrometeorological technique. Todd (2001) used a network of open-path fourier transform infrared (FTIR) optical ray method to measure ammonia emission rates from the hog lagoon.

Other investigations have developed and utilized theoretical models to study ammonia emissions from animal waste and soil. Koelliker and Minor (1973) developed a desorption model for ammonia emissions using the two-film theory. Liang et al (2002) developed mathematical model to study ammonia emissions from swine waste lagoons. The overall mass transfer coefficient in this model depends on wind velocity and temperature and was based on an old study (Halsam et al., 1924). This gives an emission of zero under calm conditions with no wind. Asman et al. (1998) reviewed the ammonia research, including process description and emission factors for ammonia emissions. Olsen and Sommer (1993) modeled ammonia emissions from stored slurry considering the effects of wind speed and surface cover. A model to predict ammonia volatilization from flooded soils using TAN, pH, temperature, floodwater depth and wind speed was developed by Jayaweera and Mikkelsen (1990). Another model to predict ammonia volatilization from manure pits in swine buildings was used by Zhang et al. (1994). De Visscher et al. (2002) developed a two layer model to study emissions from an anaerobic lagoon. The model uses effluent concentration, water temperature, wind speed and effluent pH. Aneja et al. (2001a) developed a coupled mass transfer and chemical reactions model and an Equilibrium model (hereafter called the Coupled model and Equilibrium model) to simulate ammonia emissions from swine waste lagoons. These models are based on the two-film theory of molecular transfer of ammonia across the lagoon-air interface. But the Coupled model takes into account pseudo-first order reaction of ammonia with water and acidic species (H_2SO_4 , HNO_3 , HCl) in the atmosphere, while it incorporates the effect of lagoon temperature, pH, and TAN, air temperature, wind speed, and ambient ammonia concentration. This model shows exponential increase with lagoon temperature and pH and linear increase with wind speed and TAN.

In this study, we have made comparisons of measured ammonia emission fluxes from swine waste treatment lagoon systems and modeled ammonia fluxes using both the

Coupled and Equilibrium models developed by Aneja et al. (2001a). Such a comparison of measured and modeled emission fluxes can be used to test and validate these models. The results of this study can be utilized to estimate emissions from a large number of farms and can help us to develop an ammonia budget of a region containing those farms.

2.2 Sampling and Measurements

2.2.1 Sampling Locations and Periods

As a part of project OPEN (Odor, Pathogens and Emissions of Nitrogen) ammonia flux measurements were made at 11 swine farm operations in eastern North Carolina. The waste from the hog sheds was flushed out with recycled lagoon water and discharged back into the waste lagoon from the top, often with additional treatment using potential Environmentally Superior Technologies (ESTs). Each farm was sampled during two selected periods, one representing the warm season and the other representing the cold season. The list of farms and the month for the sampling times are given in Tables 2.1a and 2.1b. Each farm was sampled for 8-10 days in each season. Only the lagoon component of hog farm was investigated in this study. Few farms have two lagoons, which are identified as suffix A and B after the farm number. Mean of observed flux and other parameters for different seasons is given in Tables 2.1a and 2.1b. Fifteen minutes averaged measurements were made for ammonia flux and environmental data. This data was then averaged to one hour period for use in this study.

2.2.2 Instrumentation and Measurements

A flow through dynamic chamber system with a variable-speed continuous impeller was used to measure NH_3 emissions from lagoon surfaces (Aneja et al., 2000; Chauhan 1999; Kim et al., 1994). The translucent plastic cylindrical chamber is 45.7 cm high and has a diameter of 25 cm (a volume of 24.34 L). The chamber was fitted into a circular hole cut in the center of a floating platform (1.2 m \times 1.2 m). The cylinder penetrated into the lagoon to a depth 7cm below the surface. The inside surface of the chamber was lined with a 5mil fluorinated ethylene propylene (FEP) Teflon sheet. A variable speed motor driven Teflon impeller was used to continuously mix the air inside the chamber. A carrier gas of compressed zero-air travels into the chamber through 0.635

cm outer diameter Teflon lines at a known flow rate between 4-8 lpm set by a mass flow controller and monitored by a data logger. The sample air from the chamber, containing ammonia emitted from the water surface, travels through 0.635cm Teflon tubing to the detection instrument. This whole system is lined with Teflon or stainless steel fitting in order to minimize chemical reactions with the sample flow. There is some concern, however, about the artificial environment within the chamber which is different from the open atmospheric conditions, particularly mean winds and turbulence, over the lagoon surface. We tried to adjust the impeller speed with the ambient wind speed at the top of the chamber. But, it is not possible to exactly match the turbulence inside the chamber with ambient turbulence above the lagoon surface. The impeller speed was set between 20 and 40 rpm.

A Thermo Environmental Instrument Incorporated (TECO) Model 17C chemiluminescence ammonia analyzer was used to monitor ammonia concentration during ammonia flux measurement periods. The sample stream entering the analyzer is divided into 3 paths. The first path mixes the sample with ozone, and all of the nitric oxide in the sample reacts with ozone and yields nitrogen dioxide. The second path passes through a molybdenum converter (325 °C) which converts all the reactive oxidized forms of nitrogen (NO_y) to nitric oxide. This sample then reacts with ozone to quantify the concentration of all oxides of nitrogen. Third sample line passes through stainless steel converter (750 °C) which converts all nitrogen oxides and ammonia into nitric oxide, which gives total nitrogen (N_T). The sample stream alternates between three flow paths. Ammonia concentration is calculated by the difference between total nitrogen and total oxides of nitrogen as

$$[\text{NH}_3] = [\text{N}_T] - [\text{NO}_y] \quad (1)$$

Ammonia analyzers were located in our temperature controlled mobile laboratory, which is maintained to be within the operating range of the instruments.

A 10 m meteorological tower was erected at each site to measure wind speed and direction, temperature and relative humidity. A Met One Instruments Model 034B-L Windset was used to measure wind speed and direction at 10 m above the surface. Air temperature and relative humidity (RH) measurements were made at 2 m height with a model HMP45C temperature and relative humidity probe housed in a radiation shield.

A CSI Model 11-L50 Innovative Sensors pH probe continuously monitored lagoon pH and C107 temperature probes measured lagoon temperature simultaneously inside the chamber. These pH and temperature probes were submerged in the lagoon at depths of 15-20 cm. Lagoon water samples were collected daily from measurement sites and were analyzed for Total Kjeldahl Nitrogen (TKN) using a digestion procedure, which converts all organic and reduced nitrogen in the lagoon samples to NH_4^+ . The NH_4^+ concentration in the sample was then determined by colorometry. A Campbell Scientific CR23X Datalogger (PC208W software) was used continuously to collect data from all the instruments. Measurements were made continuously over the measurement period and data were averaged over 15 minutes and recorded at 15-min intervals during the sampling period.

2.3. Mass Transport models

Two process-based models were developed by Aneja et al. (2001a) to determine ammonia flux from a lagoon-air interface. The principle characteristic of these models are the two thin layers or films of air and liquid (Figure 2.1) above and below the air-liquid interface for molecular exchanges between water and air, respectively (Whitman and Davis, 1923; Cussler 1996). Each layer of thickness t_i (for liquid phase $t_i = t_L$ and for air $t_i = t_a$) extends from air-liquid interface to the well mixed region of turbulent transfer in the interior of the lagoon and atmosphere, respectively. All the resistance to mass transfer across the interface is due to the thin layer in which molecular transfer takes place.

2.3.1 Basic Diffusion Equation and its Solutions

The steady state molecular diffusion equation for a horizontally homogenous thin layer in the liquid or gas (air) adjacent to the air-liquid interface is given by Arya (1999);

$$D_i \frac{d^2 C_i}{dz^2} = k_{ri} C_i \quad (2)$$

where C_i is the concentration of the diffusing material, z is the vertical distance from the interface, D_i is the molecular diffusivity, and k_{ri} is the reaction constant for ammonia in the liquid or gas phases such that $D_i = D_L$ and $k_{ri} = k_{rL}$ for liquid and $D_i = D_a$ and $k_{ri} = k_{ra}$

for air, respectively. Liquid and gas phase reactions used in this study are further discussed in section 3.2 and 3.3. Equation (2) is a second order differential equation, whose general solution is,

$$C(z) = A \exp(r_i z) + B \exp(-r_i z) \quad (3)$$

where, $r_i = \sqrt{\frac{k_{ri}}{D_i}}$ and the subscript i can be read as L for liquid and a for air. Constants

A and B can be evaluated using the following boundary conditions for the liquid and gas (air) films, respectively:

$$\begin{aligned} z = 0; C_L(0) &= C_L \\ z = t_L; C_L(t_L) &= C_{Li} \end{aligned} \quad (4)$$

$$\begin{aligned} z = 0; C_a(0) &= C_{ai} \\ z = t_a; C_a(t_a) &= C_a \end{aligned} \quad (5)$$

Solution for the concentrations in liquid and air films can be derived as

$$C_{(z)} = \frac{C_{Li} \left(e^{r_L z} - e^{-r_L z} \right) - C_L \left(e^{(z-t_L)r_L} - e^{-(z-t_L)r_L} \right)}{e^{r_L t_L} - e^{-r_L t_L}} \quad \text{for } 0 < z \leq t_L \quad (6)$$

$$C_{(z)} = \frac{C_a \left(e^{r_a z} - e^{-r_a z} \right) - C_{ai} \left(e^{(z-t_a)r_a} - e^{-(z-t_a)r_a} \right)}{e^{r_a t_a} - e^{-r_a t_a}} \quad \text{for } 0 < z \leq t_a \quad (7)$$

In which C_{ai} and C_{Li} are related by the Henry's law constant as

$$C_{ai} = H C_{Li} \quad (8)$$

Another condition to be satisfied by Eqs. (6) and (7) is that fluxes (J_i) at the interface in both the liquid and air film must be equal, i.e.,

$$J_i = -D_L \left(\frac{dC}{dz} \right)_{z=t_L} = -D_a \left(\frac{dC}{dz} \right)_{z=0} \quad (9)$$

Using the above condition, C_{Li} can be determined as

$$C_{Li} = \frac{2D_a C_a r_a (e^{r_{Li}t_L} - e^{-r_{Li}t_L}) + 2D_L C_L r_L (e^{r_{aL}t_a} - e^{-r_{aL}t_a})}{HD_a r_a (e^{r_{aL}t_a} + e^{-r_{aL}t_a})(e^{r_{Li}t_L} - e^{-r_{Li}t_L}) + D_L r_L (e^{r_{aL}t_a} - e^{-r_{aL}t_a})(e^{r_{Li}t_L} + e^{-r_{Li}t_L})} \quad (10)$$

Therefore, the ammonia flux (J) at top of the air film is determined by the following relationship

$$J = -D_a (dC/dz) \text{ at } z = t_a \quad (11)$$

Substituting from Eqs. (7) and (8) into Eq. (11),

$$J = -D_a r_a \left[\frac{C_a (e^{r_{aL}t_a} + e^{-r_{aL}t_a}) - 2HC_{Li}}{e^{r_{aL}t_a} - e^{-r_{aL}t_a}} \right] \quad (12)$$

In which C_{Li} is determined from Eq (10) .

2.3.2 Equilibrium Model

Equation (12) is an expression of ammonia flux considering chemical reactions of ammonia in both the liquid and air films. If we neglect chemical reactions in the two films, the above expression would reduce to a simpler form for an equilibrium model. For negligible reactions of ammonia in liquid and air films, reaction terms $r_{aL}t_a$ and $r_{Li}t_L$ will be very small and a Taylor series expansion can be applied for exponential terms in the above equation for the negligible chemical reactions. Thus, for the Equilibrium model, the ammonia flux is given by

$$J = -K(C_a - HC_L) \quad (13)$$

where $K = 1/(H/k_L + 1/k_a)$, is the overall mass transfer coefficient ($m s^{-1}$).

k_L and k_a are the mass transfer coefficients for ammonia in liquid and air films respectively and H is the Henry's law coefficient. Mass transfer coefficients were used from Mackay and Yeon (1983), who calculated mass transfer coefficients as functions of wind speed (at 10m height) in the form of friction velocity and Schmidt number for each phase. Henry's law coefficient was calculated by Hales and Drewes (1979).

2.3.3 Coupled Mass Transfer with Chemical Reactions Model (Coupled model)

This model takes into account molecular diffusion and some chemical reactions. In the liquid film, only ammonia's reversible reaction in the water is considered, and pH is assumed constant. Using the following chemical reaction of ammonia in the liquid phase,



Theoretical results of Olander (1960) can be used to determine the ammonia flux (J_i) in the liquid phase at the air-liquid interface

$$J = \frac{D_A}{t_L} (C_L - C_{Li}) \left(1 + \frac{D_A}{D_C} \times K^*_L \right) \quad (15)$$

Here A denotes ammonium (NH_4^+) and C is ammonia (NH_3); D_A and D_C are the diffusivities of ammonium and ammonia in the liquid phase, respectively. C_L and C_{Li} are ammonia concentrations in the bulk of the liquid phase and at the interface, respectively, and

$$K^*_L = \frac{K_{\text{NH}_4^+}}{[\text{H}^+]}, \text{ is a dimensionless parameter in which } K_{\text{NH}_4^+} \text{ is the equilibrium constant for}$$

the equilibrium equation of ammonium in the liquid, and $[\text{H}^+]$ is the concentration of hydrogen ions calculated from pH. Equilibrium constant is temperature dependant and was calculated from equation given by Jayaweera and Mikkelsen (1990).

From Eq.(9), at the liquid-air interface, fluxes can be calculated as

$$J = \frac{D_A}{t_L} (C_L - C_{Li}) \left(1 + \frac{D_C}{D_A} \times K^*_L \right) = -D_a \left[\frac{dC}{dz} \right]_{z=0} \quad \text{at } z = 0 \quad (16)$$

where C is the concentration in the air film as determined by Eq. (7).

Using Eqs (7) and (8), ammonium concentration at the liquid-air interface is given by

$$C_{Li} = \frac{\frac{2D_a C_a r_a}{e^{r_a t_a} - e^{-r_a t_a}} + C_L \times \frac{D_A}{t_L} \times \left(1 + \frac{D_C}{D_A} \times K^*_L \right)}{\text{HD}_a r_a \times \left(\frac{e^{r_a t_a} + e^{-r_a t_a}}{e^{r_a t_a} - e^{-r_a t_a}} \right) + \frac{D_A}{t_L} \times \left(1 + \frac{D_C}{D_A} \times K^*_L \right)} \quad (17)$$

The value of C_{Li} from Eq. (17) is used in Eq. (12) to calculate ammonia flux.

For the air film, the primary reactions of ammonia with sulfuric acid (H_2SO_4), nitric acid (HNO_3), hydrochloric acid (HCl), water, and the hydroxyl radical (OH) are considered (Finlayson-Pitts and Pitts, 2000; Warneck, 1999). In the air film, these five compounds are assumed to have constant concentrations, giving an effective first order reaction for ammonia, with first order reaction rate constant of ammonia in the gas phase, k_{ra} . Concentrations of these compounds were used from McColloch et al. (1998).

2.4. Results and Discussions

2.4.1 Sensitivity Analysis of Equilibrium and Coupled Models

The Coupled mass transfer and chemical reaction model and the Equilibrium model show strong dependence on lagoon temperature, lagoon pH, total ammoniacal nitrogen (TAN) and wind speed. Aneja et al (2001a) performed a sensitivity analysis of both the models with respect to physical and chemical parameters affecting ammonia flux. Lagoon temperature, pH, TAN, wind speed, air temperature, and ambient ammonia concentration were used to study their effects on ammonia flux. Lagoon temperature, pH, and TAN as well as wind speed were found to have significant effects on ammonia flux, while air temperature and ambient ammonia concentration did not show any significant effect on the ammonia flux for both the models. Model simulations show that as long as lagoon temperature remains constant, an increase of air temperature (T_{air}) from 5 to 40 °C yields a corresponding decrease in ammonia flux of less than 0.1% for both the models. This is mainly because the effect of atmospheric stability on the mass transfer coefficient is ignored in both the models. The variation in ambient ammonia concentration from 1 to 100 ppmv also gives flux changes of less than ~0.1%.

The modeled ammonia flux increases exponentially with the increase in lagoon temperature. Lagoon temperature affects the Henry's law coefficient, the liquid phase diffusivity of ammonia and ammonium, the dissociation constant, and viscosity and density of the liquid layer. The pH of a waste treatment lagoon controls the chemical equilibrium between ammonia and ammonium, and an increase in pH increases the fraction of ammonia in the solution. With an increase in pH, both models show an exponential increase in ammonia flux. Lagoon TAN controls the concentration of ammonia in lagoon water. Any increase in lagoon TAN gives a corresponding linear

increase in ammonia flux. Since the air film is a laminar sub-layer, it is affected by meteorological and environmental parameters such as wind speed and stability. Thus wind speed may also affect ammonia emissions. Sensitivity analysis of both models show a polynomial (nonlinear) relationship between ammonia flux and wind speed.

2.4.2 Comparison of Model Predictions with Observations

Ammonia flux and most of the lagoon and environmental data were averaged over 15 minute intervals during the measurements periods for both the warm and cold seasons. But for the present analysis, those data were further averaged for 1 hour periods. Although flux measurements were made for longer periods, only those hourly data are used for which all the required meteorological parameters (wind speed and air temperature) and lagoon parameters (lagoon pH, lagoon temperature and total ammoniacal nitrogen) were available. The numbers of hourly data used varied from lagoon to lagoon ranging from 11 hours to 160 hours. The total number of hours of data used from all the lagoons in this study is 1574 hours, which includes 706 hours of data for the warm season and 868 hours of data for the cold season.

Tables 2.1a and 2.1b give averages of wind speed, lagoon temperature, TAN, lagoon pH, air temperature, ammonia flux and measurement period for each lagoon during the warm and cold seasons, respectively. Average lagoon temperatures ranged from 5.0 °C to 19.0 °C in the cold season and from 17.9 °C to 29.8 °C in the warm season. Average wind speed ranged from 0.7 m/s to 5 m/s. Average TAN ranged from as low as 37 mg/l to as high as 1121 mg/l. With a few exceptions, however, TAN mostly ranged between 300 mg/l and 600mg/l. Average lagoon pH had a narrow range from 6.9 to 9.1. Average lagoon pH and TAN varied from lagoon to lagoon, but did not vary much during any given measurement period. Although air temperature varied a lot at each farm, it did not have any significant direct effect on ammonia flux as seen in our sensitivity studies. Of course, air temperature, in conjunction with other meteorological parameters, essentially determines the lagoon temperature which strongly affects the ammonia flux.

Observed ammonia fluxes were generally lower at low lagoon temperatures during the cold season than during the warm season with higher lagoon temperatures. This is because ammonia flux increases exponentially with increasing lagoon

temperature. But there were a few exceptions (e.g., Farm 4-A and Farm 2-A lagoons), when ammonia flux was higher during cold season than during the warm season. Higher values of lagoon pH, TAN and wind speed in cold season might explain these exceptions. Lagoon temperature, pH, TAN, wind speed and air temperature are used as input to the Coupled and Equilibrium models to predict ammonia flux. Ambient ammonia concentration is also needed as an input to the Coupled and Equilibrium models. It was measured at 10 m height on a few farms only. As ambient ammonia does not have any significant effect on ammonia emission flux, an average value of 150 ppb was used for all calculations.

Models were run for both the warm season and cold season data. Each model's predicted fluxes were plotted against the hourly observed flux data from the dynamic flow through chamber system. Figures 2.2-2.3 show these scatter plots of model predicted versus observed fluxes for both warm and cold seasons. A best fit line with X and Y representing the observed and modeled fluxes, respectively, is shown with the intercept set to zero, R^2 is also given for each plot.

Figures 2.2a and 2.2b compare the observed flux with the Equilibrium model predictions during the warm and cold season, respectively. Correlations between the two were moderate with $R^2 = 0.34$ and 0.35 , and slopes of the best fitted line are 0.99 and 1.01 in warm and cold season, respectively. For the entire data set for both seasons (scatter plot not shown), $R^2 = 0.34$, and slope = 0.99 . Figures 2.3a and 2.3b compare the Coupled model predictions with observed ammonia fluxes with R^2 values of 0.35 and 0.45 and slopes of 1.96 and 1.61 for warm and cold season, respectively. For the combined data (scatter plot not shown), $R^2 = 0.36$ and slope = 1.90 . Comparing the slopes of the best fitted lines with zero intercept for the two models, the Coupled model is found to significantly overpredict observed fluxes, while the Equilibrium model shows no significant bias.

Some of the predicted fluxes by both models were exceptionally high in the warm season when observed fluxes were higher than $5000 \mu\text{g NH}_3\text{-N m}^{-2} \text{ min}^{-1}$. These high ammonia fluxes could be due to the combined effect of high pH and lagoon temperature, as was observed at Harrells farm where average pH was 8.6 and average lagoon temperature was $29 \text{ }^\circ\text{C}$. Ammonia flux increases exponentially with increase in pH or

lagoon temperature. The scales of the Y-axis in Figures 2.2a and 2.3a have been set to show the scatter of lower flux values, but the best fit lines take into account all the predicted values including the exceptionally high fluxes not shown in these plots.

Some of the predicted fluxes by both models in the warm season were exceptionally low as compared to observed fluxes. These low ammonia fluxes could be due to effect of low pH and low wind speed whose effects may not be fully and accurately accounted for in the two models.

2.4.3 Other Model Performance Statistics

Various statistical measures have been proposed and utilized for evaluating the performance of air quality and dispersion models (see e.g., Irwin, 1983). Here, we have used a few simple statistical parameters, such as mean bias (MB), normalized mean bias (NMB), and normalized root-mean-square error (NRMSE), defined as

$$MB = \bar{P} - \bar{O} = \frac{1}{N} \sum_{i=1}^N (P_i - O_i) \quad (18)$$

$$NMB = (\bar{P} - \bar{O}) / \bar{O} \quad (19)$$

$$NRMSE = \frac{1}{\bar{O}} \left[\frac{1}{N} \sum_{i=1}^N (P_i - O_i)^2 \right]^{\frac{1}{2}} \quad (20)$$

where \bar{P} and \bar{O} denote the overall mean predicted and observed fluxes, P_i and O_i are the predicted and observed hourly fluxes, respectively, and N is the number of hourly observations. The above statistics were calculated for both the warm and cold seasons, separately, as well as for the combined data set. NMB and NRMSE are dimensionless parameters given as fraction in this study.

Table 2.2 compares the mean flux, mean bias, normalized mean bias and normalized root-mean-square-error (NRMSE) for both the Equilibrium and Coupled models. Under warm conditions, observed mean flux lies between the predicted fluxes by the two models. Average predicted fluxes in the warm season are 1150.8 $\mu\text{g NH}_3\text{-N m}^{-2} \text{ min}^{-1}$ and 2210.8 $\mu\text{g NH}_3\text{-N m}^{-2} \text{ min}^{-1}$ by the Equilibrium and Coupled models,

respectively, whereas the observed flux was $1545.1 \mu\text{g NH}_3\text{-N m}^{-2} \text{ min}^{-1}$. Standard deviation is also given as a measure of uncertainty. It can be seen that both model show higher uncertainty in ammonia flux prediction during warm season as compared to cold season and standard deviation in Coupled model predictions was higher than Equilibrium model. This is because some predicted fluxes were exceptionally high in the warm season. These special cases would be discussed in next section. The average bias in the Equilibrium model predictions is a negative with value of $-394.3 \mu\text{g NH}_3\text{-N m}^{-2} \text{ min}^{-1}$, while the Coupled model predictions give an average bias of $665.7 \mu\text{g NH}_3\text{-N m}^{-2} \text{ min}^{-1}$. The corresponding values of NMB are -0.26 and 0.43 . NRMSE in the Equilibrium and Coupled model predictions in the warm season are 1.76 and 3.58 , respectively. In the cold season, mean predicted fluxes by the Equilibrium and Coupled models are $944.8 \mu\text{g NH}_3\text{-N m}^{-2} \text{ min}^{-1}$ and $1391.3 \mu\text{g NH}_3\text{-N m}^{-2} \text{ min}^{-1}$, respectively, as compared with the mean observed flux of $538.1 \mu\text{g NH}_3\text{-N m}^{-2} \text{ min}^{-1}$. Both models are overpredicting ammonia flux during the cold season with NMB values of 0.76 and 1.59 for the Equilibrium and Coupled models, respectively. Normalized mean Bias in model predictions is higher in the cold season as compared to warm season. Predicted fluxes by the Equilibrium model gave NRMSE of 1.96 in cold season, while the Coupled model gave NRMSE of 2.69 . The Equilibrium model gave higher NRMSE in the cold season while the Coupled model gave higher NRMSE in the warm season. For the combined data set, Equilibrium model predictions yielded $\text{NMB} = 0.05$ and $\text{NRMSE} = 2.01$, and Coupled model predictions gave $\text{NMB} = 0.78$ and $\text{NRMSE} = 3.90$. These model performance statistics indicate slight superiority of the simpler Equilibrium model over the more complicated Coupled mass transfer with chemical reactions model. Percentages of hourly model predicted fluxes that are within a factor of two of the observed hourly fluxes are comparable for the two models; these are less than 45% . We have examined separately the cases of gross over and under predictions (by more than a factor of 5) by the Equilibrium model.

Data points in Equilibrium model predictions where predictions were greater than observed ammonia flux by the factor of five or lower than the observed ammonia flux by the factor of five were selected. There were 166 out of 868 such over predictions in the cold season while 200 out of 706 such under predictions in the warm season. Lagoon and

meteorological parameters for these data points were averaged and compared to seasonal averages of these parameters. In the warm season, TAN and pH averages, corresponding to these under predictions, were lower than the seasonal averages. TAN average was 234.4 mg/l as compared to the warm season average of 353.2 mg/l while pH was 7.1 as compared seasonal average of 7.8. The Equilibrium model predicts very low ammonia flux at low pH as ammonia flux shows an exponential increase with pH. This under prediction by the Equilibrium model in the warm season may be because of low pH. In the cold season, wind speed and pH averages for these data points were higher than seasonal averages, while lagoon temperature and TAN averages were comparable. Wind speed was 4.5 m/s as compared to cold season average of 2.6 m/s, while pH was 8.5 as compared to cold season average of 8.2. Ammonia flux in the Equilibrium model shows polynomial (non-linear) increase with increase in wind speed. This high wind speed and pH could be the reason for this over prediction in the cold season. It is possible that pH and wind speed effects may not be fully and accurately accounted for in the model. A more likely cause for the discrepancy in measured and modeled fluxes is the limited range of the impeller speed used for flux chamber measurements. Measured fluxes might be subjected to larger errors under both the strong and light wind conditions, so that model would apparently “overpredict” compared to the chamber-measured fluxes when winds were strong, and “underpredict” when winds were weak.

2.5. Conclusions

Ammonia flux measurements were made on swine waste treatment lagoons using a dynamic flow through chamber system. Hourly averages of wind speed, lagoon temperature, TAN, lagoon pH and air temperature were used as inputs into the two thin-film mass transfer models to predict ammonia flux and these predictions were compared with hourly averaged values of measured ammonia flux. Measurements made in the warm and cold season were analyzed and modeled separately to look into the seasonal differences between measured and predicted ammonia fluxes. Measured ammonia fluxes were higher in the warm season as compared to the cold season as high lagoon temperatures in the warm season lead to increased ammonia fluxes.

Both the Equilibrium model and the Coupled mass transfer with chemical reactions model predicted ammonia flux reasonably well in both seasons. Observed ammonia flux falls between predicted fluxes by the Equilibrium and Coupled models in the warm season, while both models overpredicted ammonia flux in the cold season. The Coupled model gave higher R^2 values in the both seasons, although the difference in R^2 of two models is small during the warm season. Slopes of best fit lines with zero intercept are 0.99 and 1.90 for the Equilibrium and Coupled models, respectively, indicating significant overprediction by the latter. Equilibrium model predictions gave lower value of NRMSE and bias than the Coupled model predictions in both seasons. Average of predicted fluxes by both models were within a factor of two of observed fluxes in both the warm and cold season, except by the Coupled model in the cold season when the mean was more than twice the observed flux. Considering all the hourly-averaged measurements and predictions, about 41% and 43% of the predictions by the Equilibrium and Coupled models, respectively, are found to be within a factor of two of the observations. Equilibrium model gave more consistent results as R^2 , NRMSE and bias varied less between both seasons as compared to the Coupled model results. Our assessment of the performance of the two models against the measured flux using the dynamic chamber technique should be qualified by possible measurement errors and uncertainties due to the “artificial” environment within the chamber which is different from the ambient atmospheric conditions above the open lagoon surface. The limited range of impeller speed used, in particular, might cause larger errors in the measured fluxes under both strong and light-wind conditions.

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Table 2.1a. Mean values of observed flux and other parameters during the warm season

Lagoon	Wind speed (m/s)	LagoonTemp (°C)	Air temp (°C)	TAN (mg/l)	pH	Observed flux ($\mu\text{g NH}_3\text{-N/m}^2\text{-min}$)	Time of sampling
Farm 1-A	1.2	17.9	9.1	528.5	8.0	1524.0	April 2002
Farm 1-B	2.0	19.4	17.0	401.6	8.2	1271.6	April 2002
Farm 2-A	1.4	29.8	24.5	38.0	7.6	146.2	Jun 2004
Farm 2-B	1.2	27.8	23.0	383.6	7.4	636.8	Jun 2004
Farm 3	0.7	22.8	15.2	418.0	7.5	826.2	Sep 2003
Farm 4-A	2.7	23.0	20.0	362.0	7.7	257.2	Sep 2003
Farm 4-B	0.7	22.0	20.5	229.7	8.2	1233.4	Sep 2003
Farm 5-B	1.7	28.2	23.7	303.7	7.1	2491.3	Jun 2003
Farm 6-A	2.3	29.1	26.1	647.2	8.6	6688.4	Jun 2004
Farm 6-B	2.3	26.8	24.0	171.9	8.2	3458.9	Jun 2004
Farm 7-A	2.5	24.8	22.6	157.6	6.9	1133.0	Jun 2002
Farm 7-B	2.4	26.9	25.1	37.8	8.0	454.4	Jun 2002
Farm 8-B	2.8	23.0	13.8	217.0	8.1	1213.9	Apr 2004
farm 9	1.4	24.6	23.4	371.9	8.2	1526.4	Feb 2003
Farm 10-A	2.6	22.9	21.7	1121.4	7.5	1480.4	Jun 2003
Farm 11	1.3	26.7	24.2	467.4	8.1	2034.8	Sep 2002
All Farms	1.82	24.9	21.7	353.2	7.8	1545.1	

Table 2.1b. Mean values of observed flux and other parameters during the cold season

Lagoon	Wind speed (m/s)	LagoonTemp (°C)	Air temp (°C)	TAN (mg/l)	pH	Observed flux ($\mu\text{g NH}_3\text{-N/m}^2\text{-min}$)	Time of sampling
Farm 1-A	1.7	14.8	10.1	333.7	8.6	464.5	Nov 2002
Farm 2-A	3.8	15.6	11.8	279.5	7.7	484.7	April 2004
Farm 2-B	5.0	16.3	13.3	603.0	7.7	712.8	April 2004
Farm 4-A	1.3	10.4	3.9	564.9	8.4	451.4	Dec 2003
Farm 4-B	2.6	7.1	5.0	191.9	8.7	153.2	Dec 2003
Farm 5-A	3.2	19.0	15.3	343.8	8.2	1667.7	April 2003
Farm 5-B	2.2	18.8	17.4	362.3	8.2	1622.9	April 2003
Farm 7-A	2.2	6.8	4.1	208.4	8.4	288.7	Dec 2002
Farm 7-B	2.7	6.3	1.2	53.3	9.1	148.0	Dec 2002
Farm 8-A	2.4	7.4	6.8	671.1	8.0	385.2	Feb 2004
Farm 9	2.1	5.0	4.7	637.2	8.1	265.0	Feb 2003
Farm 10-A	2.9	13.1	11.4	677.2	7.5	476.6	Mar 2003
Farm 10-B	2.1	17.9	15.5	328.9	8.2	1079.9	Mar 2003
Farm 11	3.9	7.2	6.8	558.4	8.4	134.6	Jan 2003
All farms	2.6	10.7	8.4	433.0	8.2	538.1	

Table 2.2 Statistical performance parameters for Equilibrium and Coupled models

Statistical Parameter	Equilibrium Model prediction			Coupled Model Prediction			Observed		
	Warm season	Cold season	Combined data	Warm season	Cold season	Combined data	Warm season	Cold season	Combined data
Number of Hours (N)	706	868	1574	706	868	1574	706	868	1574
Mean Flux \pm Standard deviation ($\mu\text{g NH}_3\text{-N/m}^2\text{-min}$)	1150.8 ± 3143	944.8 ± 904	1037.2 ± 2211	2210.8 ± 6086	1391.3 ± 1205	1758.9 ± 4192	1545.1 ± 1216	538.1 ± 541	989.7 ± 1037
Mean Bias ($\mu\text{g NH}_3\text{-N/m}^2\text{-min}$)	-394.3	406.8	47.5	665.7	853.3	769.1	-	-	-
Normalized Mean Bias*	-0.26	0.76	0.05	0.43	1.59	0.78	-	-	-
NRMSE*	1.76	1.96	2.01	3.58	2.69	3.90	-	-	-
% Within a Factor of 2	38	43	41	45	41	43	-	-	-

*Given in fraction form.

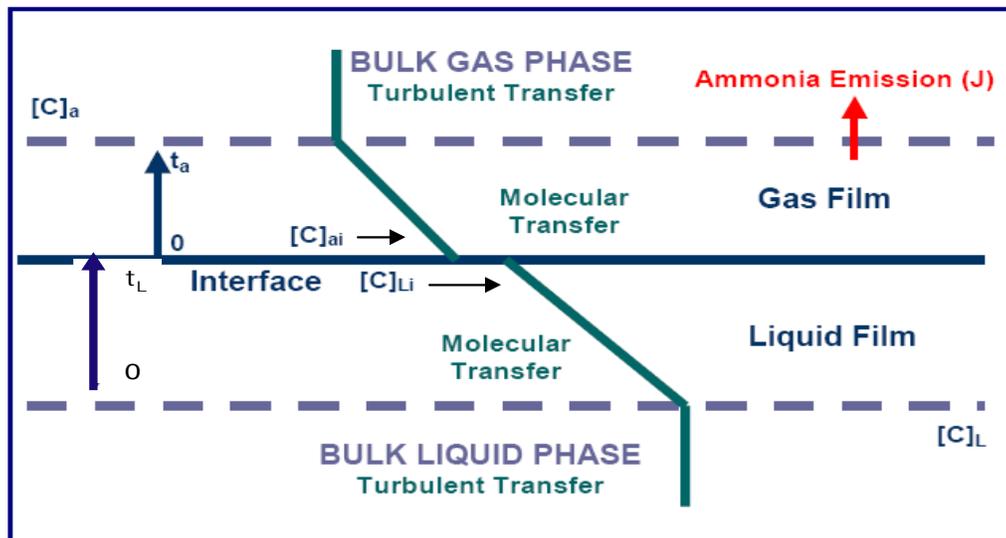


Figure 2.1. Schematic of mass transfer across liquid and gas film

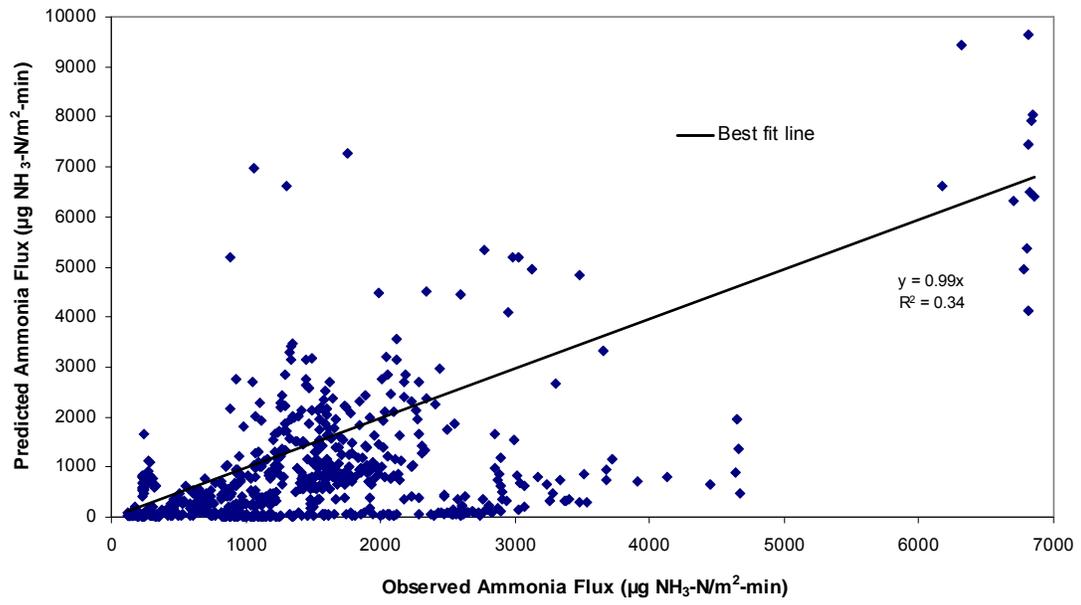


Figure 2.2a. Comparison of Equilibrium model with observed ammonia flux data with a best fit line for warm season (Some high flux data points are out of the scale shown here).

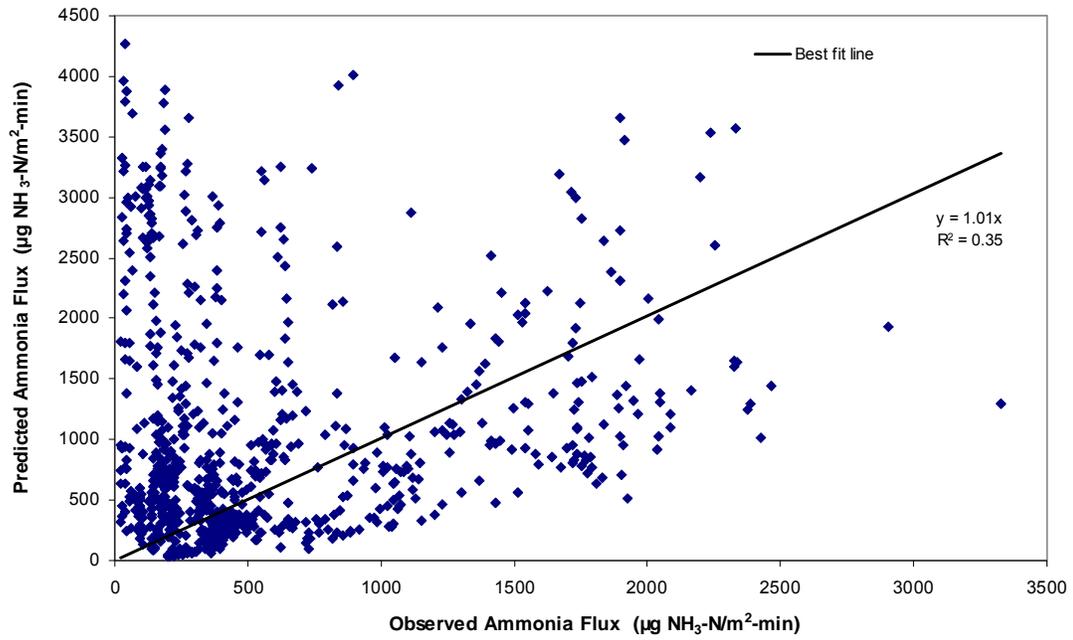


Figure 2.2b. Comparison of Equilibrium model with observed ammonia flux with best fit line in cold season.

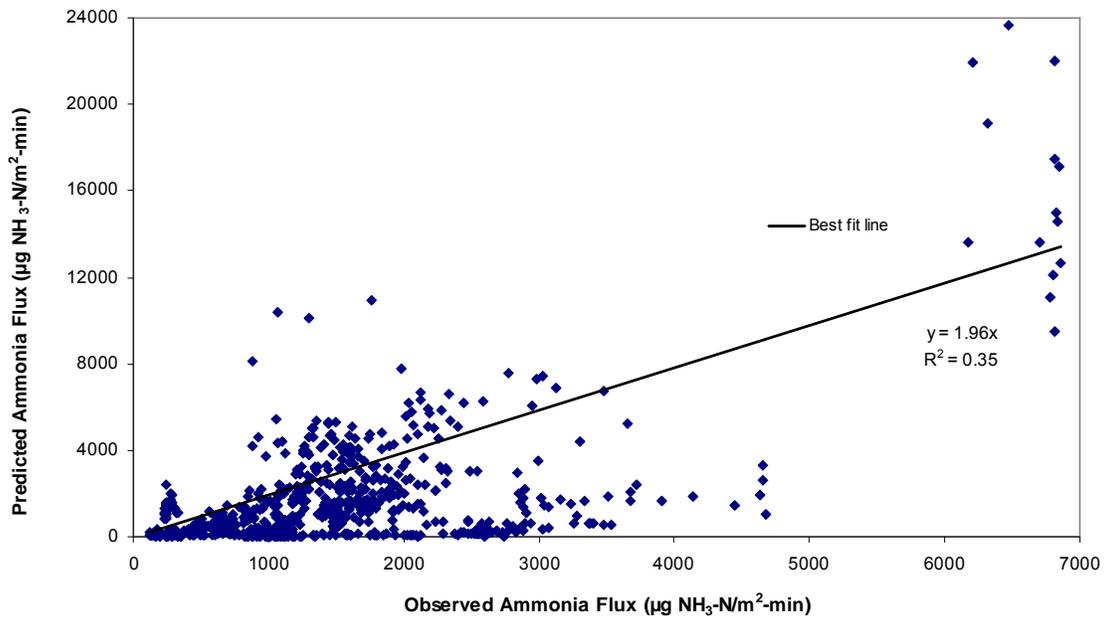


Figure 2.3a. Comparison of Coupled model with observed ammonia flux data with best fit line for warm season (Some high flux data points are out of the scale shown here).

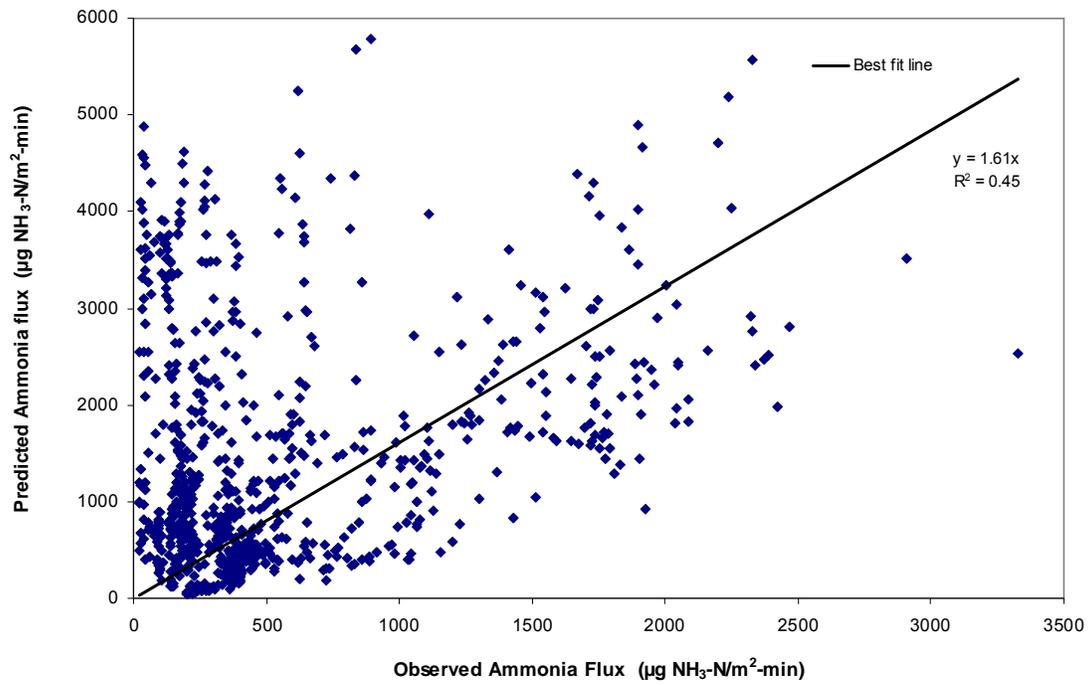


Figure 2.3b. Comparison of Coupled model with observed ammonia flux with best fit line in cold season.

CHAPTER III Modeling studies of Ammonia Dispersion and Dry Deposition studies at some Hog farms in North Carolina.

Abstract

Modeling studies have been conducted on dispersion and dry deposition of ammonia taking one hog farm as a unit. Ammonia emissions used in this study were measured under our OPEN (Odor, Pathogens and Emissions of Nitrogen) project over waste lagoon and from the barns. Meteorological data was also collected at the farm site. Actual layout of barns and lagoons on the farms was used to simulate dry deposition downwind of the farm. Dry deposition velocity, dispersion and dry deposition of ammonia were studied over different seasons and under different stability conditions. Dry deposition velocities were the highest under near neutral conditions and lowest under stable conditions. Highest deposition at short range occurs under nighttime stable conditions and lowest during daytime unstable conditions. Significant differences in deposition over crop and grass surfaces were observed under stable conditions.

3.1 Introduction

Atmospheric ammonia has become a very important trace gas in recent years. Studies have shown increasing atmospheric concentration levels of NH_3 and NH_4^+ , especially in regions of concentrated animal feeding operations (Aneja et al., 1998). On a global basis, the amount of nitrogen that enters the biosphere has nearly doubled when compared to pre-industrial times. A significant component of this increase has been in the form of ammonia-nitrogen (Galloway et al., 2001). Measurements made at National Atmospheric Deposition Program/National Trends Networks sites in North Carolina show an increasing trend in the ammonium concentration in the precipitation since 1990 (Walker et al., 2000). This increase has been linked with increasing number of hogs in North Carolina. In continents with intensive agriculture, atmospheric inputs of reduced nitrogen as ammonia and ammonium (NH_4^+) by dry and wet deposition may represent a substantial contribution to the acidification of semi natural ecosystems (Fowler et al. 1989; Grennfelt and Thornelof, 1992).

Air mass trajectories suggest that wet and dry 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 ecosystem and estuaries (Walker et al., 2000). High N-loading can have detrimental effects in terrestrial ecosystems, effects that can result in the greater export of N to surface and groundwater (Paerl, 1995). Adverse effects on sensitive ecosystems caused by high N deposition can be reduced by lowering the emissions and, to a limited extent, also by removing sources close to the ecosystem to be protected (Asman et al., 1998).

Wet and dry depositions are two pathways for removal of ammonia from the atmosphere. Data on wet deposition is available through National Atmospheric Deposition Program (NADP). There is lack of data on dry deposition of ammonia. Reliance on wet deposition measurement alone can lead to considerable underestimation (by 40-60%) of the total (wet + dry) atmospheric N deposition (Krupa and Moncrief, 2002). Modeling study by Asman (2001) found that dry deposition contributes about 66% to the total NH_x deposition to the land area of the Denmark. Gaseous ammonia undergoes dry deposition, with deposition velocities ranging up to 14 cm/s (Hanson and Lindberg, 1991; Phillips et al., 2004). Due to its high deposition velocity and its reactivity in the

atmosphere, gaseous ammonia has a relatively short atmosphere lifetime, on the order of a few days or less (Warneck, 1999). Ammonium aerosols deposit more slowly than gaseous ammonia, with deposition velocity of roughly 0.2 cm/s (Warneck, 1999). 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.

Jansen and Asman (1988) suggested that near the source, with low emission height, ground level concentrations should be higher than average, resulting in faster depletion due to enhanced dry deposition. Ammonia is mainly emitted at ground and has a relatively large deposition velocity. Different studies have been conducted to estimate ammonia deposition near the source.

According to Asman and Van Jaarsveld (1990), 20% of total ammonia and ammonium deposition takes place within 1 km of the source (animal houses), with 80-90% returning to the earth within 10 km in the form of wet and dry deposition, and remainder gets dispersed into the atmosphere for distances of several hundred kilometers. Loubet et al. (2003) studied ammonia deposition over a maize canopy using a controlled line source placed at the top of the canopy. The cumulated deposition between 12m and 162m from the source was estimated to range between 5 and 30% of the emitted NH_3 , using mass balance technique. Fowler et al. (1998) quantified the local fate livestock NH_3 emissions from poultry farm using measured ammonia concentrations and the relationship between canopy resistance and ambient ammonia concentration from intensive flux measurements. Their results show that local deposition of ammonia to woodland within 300m of the source represents 3-10% of the local emission source. Ammonia flux and deposition measurements have been made on different canopies (Sutton et al., 2000; Wyers and Erisman, 1998; Duyger et al., 1994)

Dry deposition measurements made by Walker and Robarge (2006) show that ammonia dry deposition over the nearest 500 m from the barn/lagoon complex of hog farm accounted for 11.6% of emissions with 3.5% of uncertainty, assuming 6.0 kg NH_3 /animal/yr. CMAQ simulations by Dennis et al. (2006) showed that 15-30% of the hot spot emissions deposit locally in the 12km grid cell used in simulations, while the rest can travel up to 150 -300km from the source region.

Due to local advection effects (Loubet et al., 2001), it is difficult to measure local deposition rates of ammonia with the standard micro-meteorological techniques, such as the gradient method. Many field studies to study ammonia deposition on local scale are based on the measurement of the concentration decrease with distance from the source (Duyger et al., 1994; Fowler et al, 1998; Loubet et al., 2003; Walker and Robarge, 2006). An uncertainty on fate of ammonia on local and regional scale still exists because of experimental and modeling limitations. This research is designed to study dry deposition of ammonia in the vicinity of hog farms, using a short range dispersion model. Asman (1998) showed that source height, wind speed, surface resistance, atmospheric stability, surface roughness length and surface concentration affect dry deposition of ammonia in different ways. The U.S. EPA's short range model, AERMOD, used in the present study takes into account these factors except for the surface concentration of ammonia. The objectives are to study dispersion and dry deposition patterns of ammonia downwind using the actual geometry of emission sources at the hog farm. This will help us to further understand how much ammonia gets dry deposited near the farm, and how the remaining ammonia gets transported farther away.

3.2 Methods and Materials

The U.S. EPA's recommended short range air quality model, AERMOD, is used to study dispersion and dry deposition of ammonia from hog farms. AERMOD, a steady-state dispersion model, includes the effects on dispersion from vertical variations in the PBL. In the stable boundary layer (SBL), the concentration distribution is assumed to be Gaussian, both vertically and horizontally, across the plume from a continuous point source. Gaussian distribution is also assumed in the horizontal (lateral) direction in the convective boundary layer (CBL), while the vertical concentration distribution is described with bi-Gaussian probability density functions, as demonstrated by Willis and Deardoff (1981). Buoyant plume mass that penetrates the elevated stable layer is tracked by AERMOD and allowed to reenter the mixed layer at some distance downwind. Cimorelli et al. (2005) have given a description of model formulation and boundary layer parameterization in AERMOD. The growth and structure of PBL is driven by the fluxes of heat and momentum. Depth of PBL and dispersion of pollutants within it are

influenced on a local scale by surface roughness, albedo, and available moisture. AERMOD utilizes surface and mixed-layer scaling to characterize the structure of the PBL (Cimorelli et al, 2005). AERMOD's meteorological preprocessor (AERMET) uses surface characteristics, cloud cover, upper-air temperature sounding, and at least onset of near surface measurements of wind speed, wind direction and temperature. AERMET computes friction velocity, Obukhov length, convective velocity scale, temperature scale, mixing height, and surface heat flux. AERMOD uses these scaling parameters to construct vertical profiles of wind speed, lateral and vertical turbulence, potential temperature gradient and potential temperature. Evaluations of overall model have shown that these parameterization lead to estimates of plume concentration that compare well with a wide variety of field observations (Cimorelli et al., 2005).

Dry deposition refers to the transfer of airborne material to the earth surface, including soil, vegetation, and water, where it is removed (Seinfeld and Pandis, 1998). The dry deposition flux, F_d , is calculated in AERMOD as the product of the concentration, C , and a deposition velocity, V_d , computed at a reference height, z_r as

$$F_d = C * V_d \quad (1)$$

Dry deposition velocity is calculated considering elements of meteorology and land use/surface models as used by (Walcek, 1987; Wesley et al., 2002).

$$V_d = (R_a + R_b + R_c)^{-1} \quad (2)$$

where

R_a = aerodynamic resistance (s/m)

R_b = quasilaminar sublayer resistance (s/m)

R_c = Bulk surface resistance (s/m)

Aerodynamic resistance is the resistance due to turbulence in the surface layer. AERMOD calculates aerodynamic resistance as a function of friction velocity and Obukhov length. Within the laminar sublayer over the bulk surface, transfer of ammonia is due to molecular diffusion. AERMOD calculates resistance in this layer as function of diffusivity of ammonia in air, kinematic viscosity of air and friction velocity. Within the vegetative canopy, ammonia can get deposited over the plant surface and on the soil. Ammonia can get deposited on the plant by entering through stomata or cuticles. Further resistance within the leaf could be due to mesophyll. AERMOD calculates bulk surface

resistance as a function of leaf area index, canopy stomatal resistance, canopy mesophyll resistance, canopy cuticle resistance, aerodynamic resistance in the vegetative canopy and resistance to uptake at the ground. These resistances are calculated based on parameterizations given by Wesley (2002). These parameterizations are given for different types of vegetations and for different season. These parameterizations can add to uncertainty in dry deposition velocity calculation as they are not ammonia specific. Uncertainties involved in calculation of Obukhov length and friction velocity will also contribute to the uncertainty in dry deposition velocity values.

3.2.1 Measurements

As a part of the project OPEN (Odor, Pathogens and Emissions of Nitrogen) ammonia flux measurements were made at several hog farms in eastern North Carolina. Barham farm (35.70 °N, 78.31 °W) was sampled during spring season and Moores (35.14 °N 77.47 °W) was sampled during summer and winter season. Measurements were made of ammonia flux from waste lagoons using a dynamic flow through chamber system. Barn emissions were measured using open-path Fourier transform infrared (OP-FTIR) spectroscopy. Meteorological data on ambient temperature, relative humidity (RH), wind speed and wind direction was also collected during each sampling period. These emission and meteorological data are used in modeling ammonia dispersion and dry deposition from the two farms. Upper air sounding data is used from National weather service stations. Cloud cover data was used from the nearest North Carolina State Climate Office's weather stations.

3.2.2 Model Simulations

In this study, grass and crop are used as ground covers to study dry deposition on these surfaces separately. Separate AERMET files are created for both surfaces giving respective surface characteristics. Different stability conditions are predicted by AERMET for grass and crop surfaces. The information on surface characteristics can be found in AERMET manual (USEPA, 1998). AERMOD calculations were made for both grass and crop surfaces in each season. Crop and grass dry deposition calculations are made for the same date and hour with the same wind speed at 10m height, to compare the

difference between deposition under the same wind speed and emission conditions. Deposition along the wind direction given as orientation 1 (Figure 3.1) is studied in detail and later compared to orientation 2. All other meteorological parameters were kept same, while changing wind direction only to study dispersion and dry deposition along these orientations.

Philips et al., (2004) measured dry deposition velocity of ammonia over a natural grass surface on an animal farm site over a wide range of meteorological conditions encountered during different seasons. Data on wind speed, wind direction, RH and ambient temperature was collected at 2 heights (2 m and 6 m). Ammonia concentrations were also measured at 2 m and 6 m heights using two Thermo Environmental Instruments Inc. (TEI), Model 17C chemiluminescence ambient ammonia analyzers. Modified Bowen ratio method and gradient method were used along with Monin-Obukhov similarity theory to estimate vertical flux of ammonia under different meteorological conditions. Vertical ammonia flux and ambient ammonia concentrations were used to calculate ammonia deposition velocity using Eq. (1). Meteorological data measured by Philips et al. (2004) is used to model dry deposition velocities of ammonia using AERMOD in present study. These modeled dry deposition velocities are used for comparison with observed value under same meteorological conditions.

3.3 Results and Discussion:

3.3.1 Dry Deposition Velocity

Considerable uncertainty is involved in modeling deposition of ammonia, because deposited ammonia can also be emitted back to the atmosphere. Farquhar et al (1980) explained this in the terms of ‘compensation point’, which is the air concentration at which no net in or out-flux occurs through stomata. A compensation point is expected to occur because of the presence of NH_x in plant metabolism and in soil and its equilibrium with gaseous NH_3 . Deposition of ammonia occurs when ambient ammonia concentration is higher than compensation point, otherwise there would be net emission. In particular situation, NH_3 emission may also occur from recently fertilized soils, decomposing leaves or decomposing urine from grazing animals.

Determination of compensation point requires the knowledge of soil and plant leaf chemistry. An appropriate use of compensation point in relation to ammonia exchange has been made in resistance models developed by Sutton et al., (1998). However, AERMOD assumes surface concentration of ammonia to be zero to calculate ammonia deposition flux. An important parameter in calculation of ammonia deposition velocity is cuticular resistance to ammonia. Parameterization of cuticular resistance is, however not available under North American conditions as no measurements of this resistance have been made. A simple parameterization of cuticular resistance was proposed by Sutton et al. (1998) as a function of relative humidity. This estimation of cuticular resistance was used for this study, but model predicted deposition velocities were too low when RH was low. To get deposition velocity in comparable range to measured values, a minimum cuticular resistance value was used as input to this model.

Philips et al. (2004) measured ammonia deposition velocity at a relatively flat, uniform, and smooth site with grass or short vegetation. Measurements were made for 7 to 10 days to get representative data for each season. This site was located near a small experimental hog farm with a lagoon. Dry deposition velocity is modeled using meteorological data from this experiment and using grass as vegetative cover. Table 3.1 gives a comparison between measured and modeled ammonia deposition velocities in different seasons. Average wind speed and model estimated friction velocity is also provided. Deposition velocities are divided into daytime and nighttime based on sunrise and sunset times in each season. The model under predicted deposition velocities in all seasons and at both day and night times. Daytime deposition velocities are lower by a factor of about two in spring and 3 to 5 in other seasons. Nighttime dry deposition velocities are consistently very low (0.06 to 0.09 cm/s) in all seasons. Reason for such a low calculated deposition velocity was that the aerodynamic resistance calculated by AERMOD was very high and was the dominant resistance at night. The highest deposition velocities calculated by the model are during unstable and near-neutral conditions and lowest during stable conditions. This is consistent with stability dependence of observed deposition velocities by Philips et al. (2004). Lower model calculated deposition velocities were also reported by Dennis et al. (2006) using the

CMAQ regional model. They proposed that deposition velocities of ammonia should be adjusted higher so that these are comparable to observed deposition velocities of SO₂.

3.3.2 Dispersion of ammonia

Perry et al. (2005) provides an overview of the AERMOD model's performance against the concentration observations taken from 17 field study databases. The studies include sites with flat and complex terrain, urban and rural conditions, elevated and surface releases, and with and without building wake effects. The evaluation measures were restricted to those that are relevant to regulatory applications, with an emphasis on the ability of the model to simulate the upper end of the concentration distribution. Among these databases, project Prairie Grass represented surface releases over a flat terrain rural site. AERMOD shows a tendency to underpredict the higher concentrations over this flat terrain rural site. It showed a concentration distribution that matched observations well, suggesting that the model is capable of simulating near-field dispersion from the surface releases. Robust high concentration (RHC) ratio of predicted to observed was 0.87, which also shows 13% under prediction.

Our study represents surface releases of ammonia from several point sources (exhaust fans in barns) and a finite area source (waste lagoon) at the hog farm and its dispersion over a flat rural terrain. Ammonia dispersion pattern is studied by plotting crosswind integrated ammonia concentrations against the downwind distance. Dispersion study is done with data from Barham farm, with wind direction along orientation 1 (Figure 3.1). Downwind concentrations depend on barn and lagoon emission rates, wind speed and stability condition for the given hour. Ammonia concentration is crosswind integrated at every 50m to study the decrease in concentration at 1 m height or ground level. Cross-wind integrated concentrations were normalized using the surface-layer similarity theory to study the downwind dispersion pattern. Dry deposition was not considered in this dispersion study, which means that dry deposition was assumed to be zero. Cross-wind integrated concentration (C_y) is normalized with friction velocity (U_*), roughness parameter (Z_0) and emission rate (Q). Dimensionless ground level concentration, C_0^* , is given by Van Ulden (1978)

$$C_0^* = C_{y0} U_* Z_0/Q \quad (3)$$

Where the subscript 0 indicates surface-layer scaling.

Downwind distance is made non-dimensional as X/Z_0 where X is downwind distance, and C_0^* is plotted against X/Z_0 for different values of stability parameter Z_0/L (Figure 3.2), where L is Obukhov length. Negative values of Z_0/L represent unstable conditions, positive values represent stable conditions and near zero values indicate near neutral conditions. Figure 3.2 shows normalized ground level concentrations at X/Z_0 values from 1000 to 50,000 under different stability conditions. Concentrations are high in immediate vicinity of the farm but decrease very rapidly as we move away from the farm. Further downwind concentrations are smaller and the decrease in concentration is also small. Decrease in downwind concentration is slowest under most stable conditions. Under very stable conditions ($Z_0/L = 0.031$), concentration first remains almost constant with distance and then starts decreasing. Under near-neutral conditions, decrease in concentration is faster than in stable conditions. Ground level concentration shows different pattern under unstable conditions. Slopes of C_0^* show that downwind concentration decreases more rapidly under unstable condition as compared to stable and near neutral conditions. But further downwind, ground level concentrations decrease very slowly and concentrations even become higher than those in near neutral conditions. This pattern is a result of the way the vertical distribution is treated in AERMOD under convective conditions. The vertical and lateral velocities in each element are assumed to be random variables and characterized by their probability density functions (pdf). In the CBL, the pdf of the vertical velocity (w) is positively skewed and results in a non-Gaussian vertical concentration distribution (Lamb, 1982). The positive skewness is consistent with the higher frequency of occurrences of downdrafts than updrafts. Ammonia that mixes up in the convective boundary layer keeps moving slowly toward the ground in more frequent downdrafts than updrafts. The sudden change in slope of concentration distribution under unstable conditions is due to this bi-Gaussian distribution. This pattern is consistent with the results of numerical simulations and field observations (Lamb 1982; Weil, 1988). This plot shows that concentrations at ground level in the vicinity of hog farm would be higher under stable conditions and lower under unstable conditions, for a given emission rate and wind speed conditions. But further

downwind, ground level concentrations under unstable conditions might become higher than those in near-neutral conditions.

For highly convective conditions, the mixed layer similarity theory was used to study dispersion pattern. The convective velocity scale (W_*) and mixed layer depth (H) along with wind speed (U) and emission rate (Q) are used to normalize downwind crosswind integrated concentration (C_y) and downwind distance (X), as given in Arya (1999). Normalized concentration is given by

$$C_y^* = C_y U H / Q \quad (4)$$

and downwind distance is normalized as

$$X^* = W_* X / U H \quad (5)$$

In the CBL C_y^* is plotted as a function of X^* for different stability conditions based on H/L and shown in Figure 3.3. This graph shows that under convective conditions, concentration distribution does not change much with the change in H/L . Arya (1999) discussed that normalized crosswind integrated ground level concentration initially decreases as $X^{*-3/2}$, as predicted by local free convection and free convection layer similarity theories. It attains minimum value of less than 1 and then increases and becomes constant at value of one. Similar decrease in C_y^* with X^* can be seen in Figure 3.3, where it flattens out at large distance. This could be the minimum value attained by C_y^* before it increases and becomes constant. The slopes of C_y^* vs. X^* is -1.55 and -1.72 for H/L values of -550 and -620, respectively, which are higher than expected values discussed above. Nieuwstadt (1980) also discussed the dependence of C_y^* on X^* using the measured data from the Project Prairie Grass. Van Ulden (1978) and Briggs (1978) predicted that under convective conditions C_y^* decreases as X^{*-2} . However, Nieuwstadt (1980) showed that within the convective matching region, the $X^{*-3/2}$ power law is superior to X^{*-2} dependence. Convective matching region has been defined by the $-L < z < 0.1h$ condition. Venkatram (1992) discussed the behavior of cross-wind integrated ground level concentrations under neutral, stable and unstable conditions. He found that under unstable conditions, the normalized concentration falls off as X_*^{-2} rather than $X_*^{-3/2}$ predicted by the local free convection similarity theory, where $X_* = X/L$.

The vertical profile of concentration in the plume from a near surface continuous point source in convective boundary layer was studied by Willis and Deardorff (1976)

using laboratory simulation in a convection tank. They found that the height of maximum C^* , or the plume centerline, coincides with the release height only up to a dimensionless distance $X^* \sim 0.5$, after which it lifts off rapidly, attains a maximum around $Z^* = 0.8$, and then gradually comes down to the surface. This implies a highly non-Gaussian vertical distribution of concentration for $X^* > 0.5$. We also studied the vertical profiles of concentration under convective conditions for $H/L = -550$. This vertical profile was studied for Barham farm using the wind direction orientation 1 and downwind distance was measured from the boundary of the farm. Here, C_y^* is plotted against $Z^* = z/H$ for different values of X^* (Figure 3.4). Vertical profiles show nearly exponential distribution up to $X^* \sim 0.5$, but it does not show a clear uplift of plume at $X^* > 0.5$. A slight bent in slope is visible at $X^* = 0.97$, but maximum concentration is still at the surface. Nearly uniform concentration distribution through out the PBL was reached at higher value of $X^* \sim 3.2$. This is a consequence of plume trapping between the surface and the capping inversion. Some differences between our model simulations and Willis and Deardorff's (1976) laboratory experiment might be expected due to different source geometry and configuration (an area source and multiple sources) used in our model study.

3.3.3 Ammonia Deposition

Ammonia deposition is studied downwind at two hog farms, Barham farm and Moores farm. Barham farm has two types of sources, waste water lagoon and 6 barns where hogs are housed. Moores farm has a waste water lagoon and 8 barns. Barns at both farms are forced ventilated using big fans. Barn fans are treated as point sources and lagoon is treated as an area source in this study. Meteorological data from Barham farm represent spring season and fall season whereas Moores farm data represent summer and winter conditions. Deposition of ammonia is influenced by the stability conditions, wind speed, dry deposition velocity and emission rate of ammonia for that particular hour. Three particular hours are selected to represent a set of conditions under which deposition will be studied and compared. Three hours represent different times of the day and different stability conditions and emission rates. Unstable condition with a low value of the Obukhov length is chosen to also represent high emission rate. Night time stable condition is selected with a low value of the Obukhov length and low emission rate.

Evening time near-neutral conditions are chosen with large magnitude of Obukhov length. Deposition downwind of the farm boundary is studied up to 2500m. Deposition on grass and crop surfaces has been studied separately. Table 3.2a and 3.2b give deposition of ammonia emitted from Barham farm in spring and fall seasons, respectively, over the grass and crop surfaces. Tables 3.3a and 3.3b give deposition of ammonia from Moores farm in summer and winter seasons, respectively, over the grass and crop surfaces. These tables give ammonia depositions up to 500 m from the farm and between 500 m and 2500 m and total deposition up to 2500 m. In parentheses are the depositions as percentage of total ammonia emitted for that hour.

For comparison of grass and agricultural/crop surfaces, wind speed was assumed to be the same at 10 m height on both surfaces. Since roughness length is different for grass and crop, the wind speed profile will be different over them. Bowen ratio and albedo values for grass are different for crop surface in each season, which would affect sensible heat flux. Thus the values of the Obukhov length and friction velocity are different over the two surfaces. These factors affect the dry deposition velocity calculations and deposition patterns. Bowen ratio value is higher over the crop surface when compared to the grass surface in all seasons, though the difference between the two values is small in spring season, which is the sowing season for crops in North Carolina. The crop height and leaf area index is low in spring season. In winter Bowen ratios for the crop and grass surfaces are comparable under conditions of frost or snow. Bowen ratio is high over crop surface in summer season assuming high leaf density, as crops are green and at full bloom in summer. This high Bowen ratio over the crop surface leads to lower sensible heat flux as compared to the grass surface. Roughness length is higher for crops as compared to grass surface, except in spring when crop height is small. This will affect friction velocity. These combinations of different sensible heat fluxes and friction velocities lead to different stability conditions. Thus deposition velocity and deposition pattern are expected to be different over the two surfaces.

Tables 3.2-3.3 show that Obukhov length is higher over the crop surface than the grass surface, except in spring season where it is comparable for the two surfaces. In other seasons, nighttime conditions are more stable at night for crop area and more unstable during day time hour selected for study. Deposition velocity is high in near-

neutral and unstable conditions but low in stable conditions. This trend is seen in all seasons for both crop and grassy surfaces. This trend is also observed in measurements and is discussed earlier in this paper. Difference between deposition velocities over crop and grass surfaces is very small in spring and fall seasons. In summer and fall seasons, however, deposition velocities over crops are higher than those over the grass surface.

As shown in Figures 3.1 and 3.2, ammonia ground level concentrations are large in immediate vicinity of the farm. Ammonia deposition is also high in first few hundred meters downwind of farm. Deposition up to first the 500 m is compared to that between 500 and 2500 in Tables 3.2-3.3. At Barham farm in spring season, 8.4% and 10.5% ammonia emitted from the farm gets deposited on the grass surface up to 2500 m from the farm, under unstable and near neutral conditions, respectively (Table 3.2). Out of this percentage, more than half gets deposited within 500 m of the farm. Ammonia deposition is the highest under stable conditions, where 13.3% deposition occurs within 2500 m of the farm. This number is high compared to unstable and near neutral conditions, even though deposition velocity is much lower. This is because ground level concentrations of ammonia are higher under stable conditions, due to less turbulent mixing. Also, the wind speed was lower than in unstable and near neutral conditions. This also contributes to higher deposition. Deposition under near neutral conditions could be higher as wind speed is high when compared to other stability conditions. Over the crop surface, deposition is slightly higher than that over the grass surface. Difference in total deposition up to 2500m under unstable and near neutral conditions is very small (~0.5%), but under stable conditions, deposition is 1.5% higher over crop area than the grass surface.

In fall season, total deposition (up to 2500 m) on grass surface is higher (14.1%) under stable conditions as compared to 4.3% under unstable conditions, for the same wind speed (Table 3.2b). Here the difference is larger than for spring, though the Obukhov length is also lower in fall than in spring. Deposition under near neutral conditions is 6.8%, which is in between stable and unstable conditions. Deposition velocity is high under near-neutral conditions, because wind speed is also higher in comparison to other stability conditions. The deposition velocities over crop and grass surfaces are not much different, except for the nighttime stable conditions. Same as found

for the spring season, when major portion of deposition occurs in the first 500m, except under stable condition where this contribution is lower.

Deposition study under summer conditions is done with data from Moores farm (Table 3.3a). As in spring and fall seasons, deposition is higher under stable and lowest under unstable conditions, with major portion of deposition being within 500m distance. Ammonia deposition is higher by 4% under stable conditions over the grass surface, whereas it is higher over crop surface under unstable and near neutral conditions. This could be because deposition velocity is higher over crop surface under unstable and near neutral conditions, whereas it is comparable to the grass surface under stable conditions. The difference in deposition in unstable and near neutral conditions is also higher in fall season (2.3 – 2.8%).

In winter season, ammonia deposition downwind of Moores farm shows the highest deposition of 16.6% under stable conditions over the grass surface. This could be due to smaller Obukhov length when compared to other seasons. Depositions under unstable and near neutral conditions are 4.6 and 5.1%, respectively. Under stable conditions, deposition is higher over grass surface by 4.4%, while is slightly higher over crop surface under unstable (1.2%) and near neutral (1.1%) conditions.

Ammonia deposition modeling results as discussed above, are for along the wind direction orientation 1 as shown in figure 3.1. Ammonia deposition calculations were also done along the orientation 2 as shown in figure 3.1, for both Barham and Moores farms. Comparison of results shows that the change of orientation can make a difference of up to 2.3% in ammonia deposition. This difference was more on the Barham farm than on Moores farm. Orientation 1 gave higher deposition on both the farms and in all the seasons and stability conditions.

AERMOD underestimates ammonia deposition velocity in comparison with the observed deposition velocities. This would lead to underprediction of total ammonia deposition near the farm. If we take into account this underprediction, ammonia deposition could be much higher (by the factor of 2-5) when compared with results of this study.

3.4 Conclusions:

This study was done to investigate how ammonia emitted from a hog farm disperses and gets deposited downwind of the farm. USEPA's dispersion model AERMOD was used to study the dispersion and deposition patterns of ammonia. Data on meteorological parameters and emission rate collected at two hog farms (Barham and Moores farms) was used in this study. AERMOD's meteorological preprocessor AERMET was used to create meteorological input file in the model. Dry deposition velocity and meteorological data from Philips et al (2004) were used to compare dry deposition velocity calculations by AERMOD. Modeled dry deposition velocities were smaller than the observed values, by a factor of 2 to 4 during day and upto 8 during night. These lower values are attributed to the lack of understanding of the ammonia deposition and emission from grass and crop surfaces. Observations show both the deposition and emission occurring, depending on the compensation point at the vegetation surface. Deposition parameterization in AERMOD does not account for this. Ammonia dispersion study shows that ammonia ground level concentrations are very high near the farm and decrease rapidly as we move away from the farm. This decrease in concentration with distance is small when we move further downwind of the farm. The decrease of concentration is faster under unstable conditions and the slowest under stable conditions. The rate of decrease in concentration with distance for near neutral conditions lies somewhere between those for stable and unstable conditions. Ground level concentrations would be lower under unstable conditions for a given emission rate, but become higher than the near neutral conditions at certain distance downwind due to bi-Gaussian distribution of vertical distribution under unstable conditions. Dry deposition of ammonia up to 2500 m downwind of the farm is studied under different stability conditions and over crop and grass surfaces. Major contribution to deposition as percentage of total emission comes from first 500m from the farm as ground level concentrations are very high. Deposition was the highest under stable conditions and lowest under unstable conditions. Under stable conditions, more deposition occurred over the grass surface than over the crop surface with the exception of spring season where it was higher over the crop surface. Under unstable and near neutral conditions, deposition was higher over the crop surface for winter, summer and spring seasons. These

differences between crop and grass surfaces were higher under stable condition. Wind orientation could also make a difference on the downwind deposition depending on the layout of the source on the farm. Further studies should be done by taking into account the effect of farm buildings. Study on the dry deposition of ammonia in the forest canopy downwind, if present, should also be studied. Better understanding of deposition parameterization and soil and leaf chemistry is also needed to reduce the uncertainties involved in this study.

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Table 3.1. Comparison of modeled versus measured dry deposition velocities for different seasons and times of day.

	Spring		Summer		Fall		Winter	
	Day	Night	Day	Night	Day	Night	Day	Night
Modeled (cm/s)	1.74	0.09	1.04	0.09	0.80	0.06	0.51	0.08
Measured (cm/s)	2.85	0.62	3.94	0.76	2.82	0.07	2.41	0.19
Wind speed* (m/s)	4.3	2.6	2.0	1.4	2.3	1.1	2.5	1.4
Friction velocity** (m/s)	0.4	0.2	0.2	0.1	0.14	0.03	0.11	0.02

* Wind speed at 6m height

** Model calculated friction velocity

Table 3.2a. Dry deposition of ammonia (in grams and percentage) and related parameters from Barham farm during the spring season measurement period.

	Grass			Crop		
	Stable	Near Neutral	Unstable	Stable	Near Neutral	Unstable
Monin- Obukhov Length (m)	7	-610	-21.1	6.1	-489	-18.7
Wind Speed(m/s)	2.1	5.1	3.1	2.1	5.1	3.1
Emission (g/hr)	4765	6973	6484	4765	6973	6484
Deposition velocity (cm/s)	0.09	1.71	1.49	0.09	1.68	1.42
Upto 500m Deposition	282 (5.9)	421 (6.5)	408 (5.8)	316 (6.6)	448 (6.9)	426 (6.1)
500m- 2500m Deposition	354	259	181	398	266	187
Total Deposition	636 (13.3)	680 (10.5)	589 (8.4)	714 (15)	715 (11)	612 (8.8)

Table 3.2b. Dry deposition of ammonia (in grams and percentage) and related parameters from Barham farm during the fall season measurement period.

	Grass			Crop		
	Stable	Near Neutral	Unstable	Stable	Near Neutral	Unstable
Monin- Obukhov Length (m)	5.8	-54.9	-5	8.6	-132	-12
Wind Speed(m/s)	2.6	4.2	2.6	2.6	4.2	2.6
Emission (g/hr)	3748	4406	5476	3748	4406	5476
Deposition velocity (cm/s)	0.09	1.10	0.92	0.09	1.10	0.95
Upto 500m Deposition	225 (6.0)	191 (4.3)	159 (2.9)	157 (4.2)	160 (3.6)	160 (2.9)
500m- 2500m Deposition	303	109	75	208	96	80
Total Deposition	528 (14.1)	300 (6.8)	234 (4.3)	365 (9.8)	256 (5.8)	240 (4.4)

Table 3.3a. Dry deposition of ammonia (in grams and percentage) and related parameters from Moores farm during the summer season measurement period.

	Grass			Crop		
	Stable	Near Neutral	Unstable	Stable	Near Neutral	Unstable
Monin- Obukhov Length (m)	7.1	-88.8	-6.6	11.1	-280	-18.7
Wind Speed(m/s)	2.1	4.6	2.6	2.1	4.6	2.6
Emission (g/hr)	4392	5796	5040	4392	5796	5040
Deposition velocity (cm/s)	0.09	1.14	1.06	0.09	1.94	1.76
Upto 500m Deposition	242 (5.5)	245 (4.2)	154 (3.0)	164 (3.7)	327 (5.6)	248 (4.9)
500m- 2500m Deposition	285	119	54	190	173	98
Total Deposition	527 (12.0)	364 (6.3)	208 (4.1)	354 (8.0)	500 (8.6)	346 (6.9)

Table 3.3b. Dry deposition of ammonia (in grams and percentage) and related parameters from Moores farm during the winter season measurement period.

	Grass			Crop		
	Stable	Near Neutral	Unstable	Stable	Near Neutral	Unstable
Monin- Obukhov Length (m)	3.7	-59.4	-3.7	5.7	-135.4	-8.5
Wind Speed(m/s)	2.6	5.1	2.6	2.6	5.1	2.6
Emission (g/hr)	756	936	936	576	936	936
Deposition velocity (cm/s)	0.09	0.62	0.48	0.09	0.92	0.74
Upto 500m Deposition	52 (7.0)	32 (3.4)	23 (2.5)	42 (5.5)	38 (4.1)	31 (3.3)
500m- 2500m Deposition	73	16	20	61	20	23
Total Deposition	125 (16.6)	48 (5.1)	43 (4.6)	93 (12.2)	58 (6.2)	54 (5.8)

Figure 3.1. Orientations of Barham farm and Moores farm with respect to wind direction.

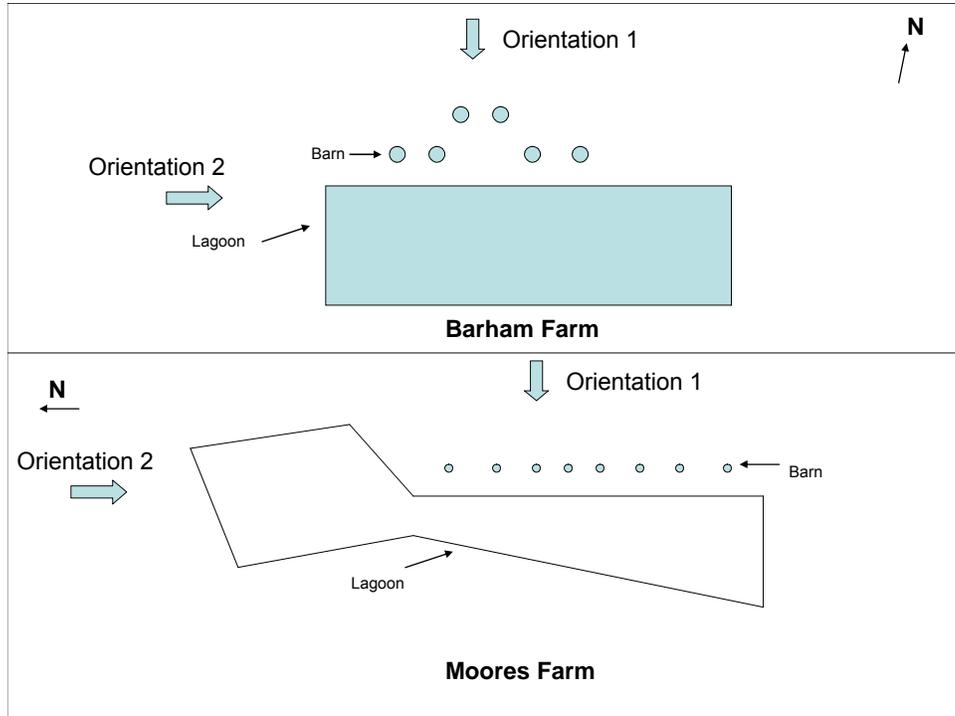


Figure 3.2. Change in dimensionless ground-level concentration with dimensionless distance for several stability conditions based on Z_0/L at Barham farm with direction along the orientation 1.

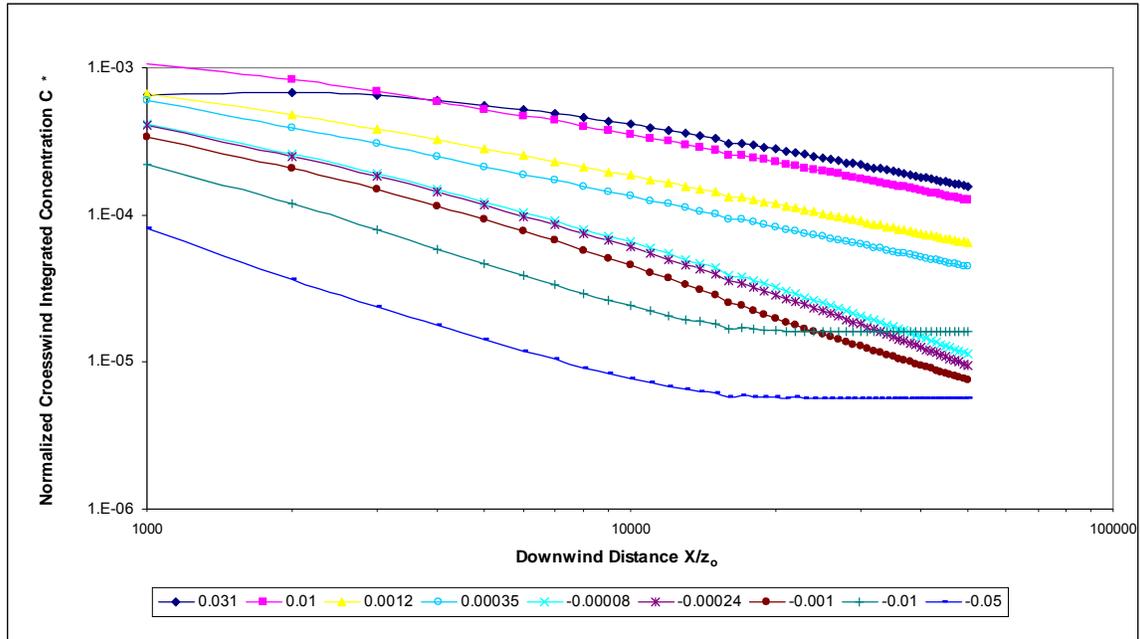


Figure 3.3. Normalized Cross-wind intergrated ground-level concentration as function of normalized downwind distance, for convective conditions based on H/L at Barham farm with direction along the orientation 1.

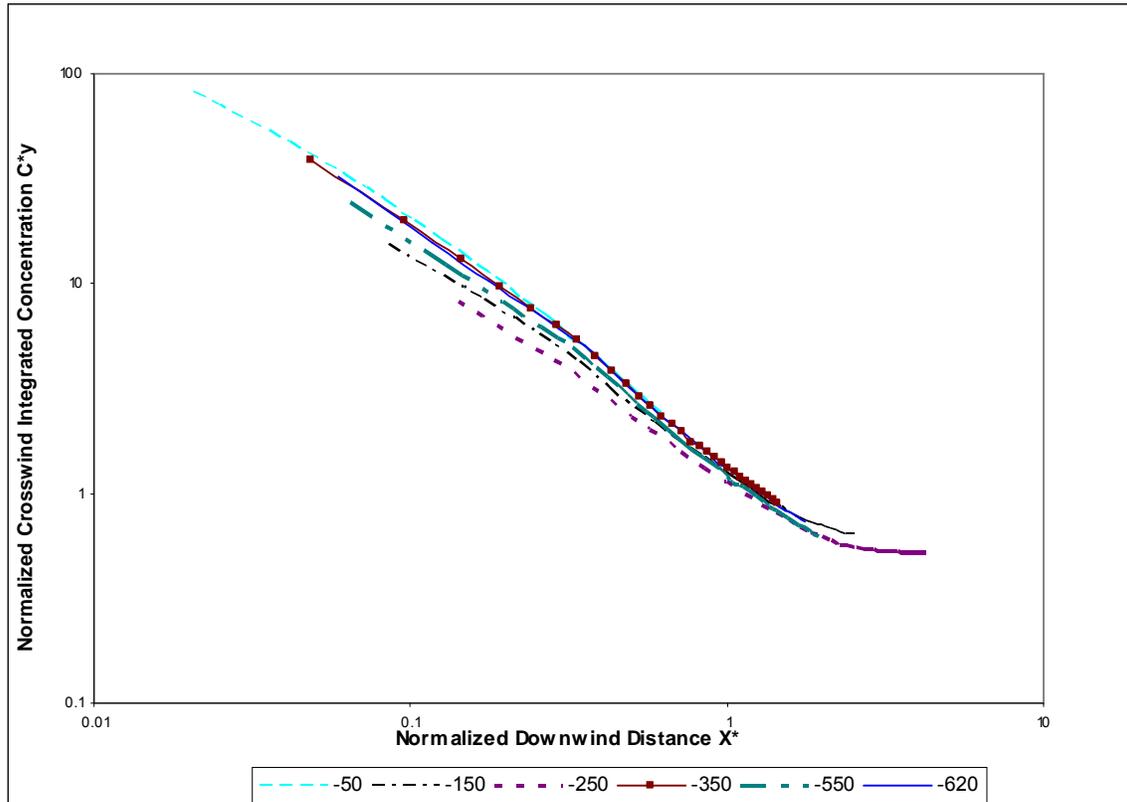
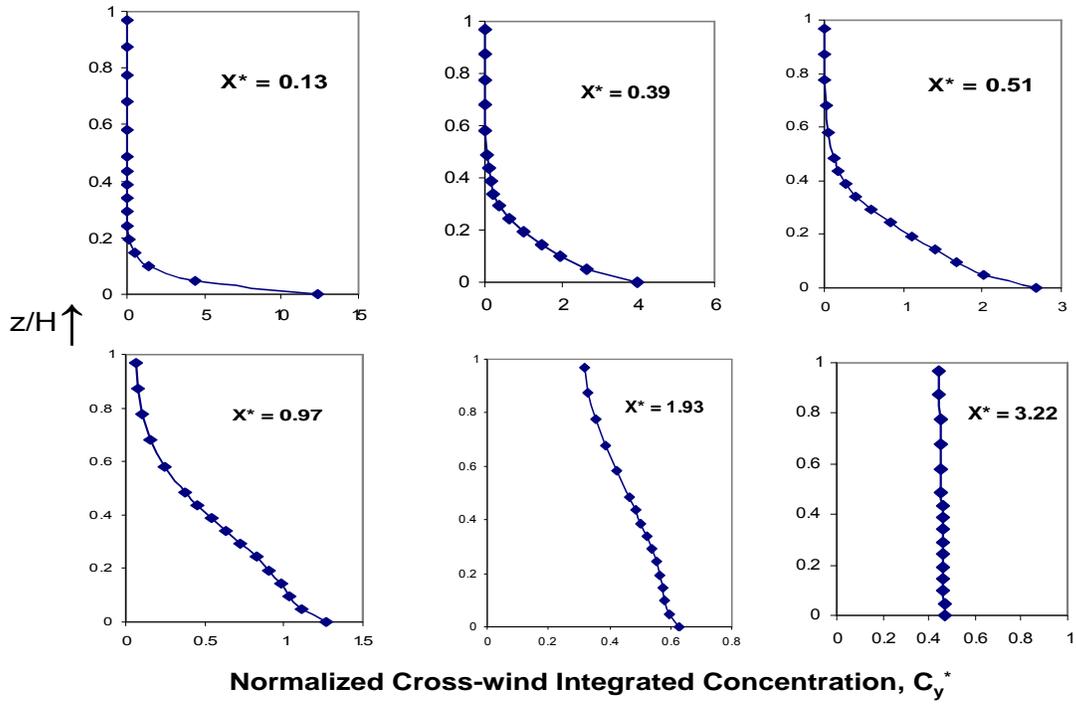


Figure 3.4. Vertical profile of normalized cross-wind integrated concentration (C_y^*) at different value of X^* .



CHAPTER IV Conclusions

Ammonia flux measurements were made on waste treatment lagoons at 11 swine farms in eastern North Carolina using dynamic flow through chamber system. At the same time, barn emissions were measured using open-path Fourier transform infrared (OP-FTIR) spectroscopy. Meteorological parameters wind speed, wind direction, ambient temperature and lagoon parameters pH, TAN and lagoon temperature were also recorded with hourly averages. Each farm was measured in warm and cold seasons to look into seasonal variation in ammonia flux. Ammonia flux was higher in warm season and lower in cold season which can be attributed to higher lagoon temperatures in warm season.

Considering molecular diffusion of ammonia across thin layers in liquid and air just below and above the air-lagoon interface, previously formulated Equilibrium model and Coupled mass transfer and chemical reactions model were used to predict ammonia flux from swine lagoons, and these predictions were compared to observed fluxes. Both models predicted ammonia fluxes reasonably well in both seasons. In warm season, the Equilibrium model underpredicted ammonia flux, while the Coupled model overpredicted the observed flux. Both models overpredicted ammonia flux in cold season. The Coupled model gave higher R^2 value in both seasons, though difference of R^2 values in warm season is small. Slopes of the best fit lines with zero intercept are 0.99 and 1.96 for the Equilibrium and Coupled models, respectively, indicating significant overprediction by the latter in warm season. Slopes during cold season were 1.01 and 1.61 for Equilibrium and Coupled model, respectively, again showing high overprediction by the Coupled model. Other statistical performance parameters were calculated for comparison of predicted and measured fluxes. Average predicted model fluxes were within a factor of

two of the observed fluxes, except in cold season when Coupled model predictions were more than twice the observed. Considering all the hourly-averaged measurements and predictions, 41% and 43% of the predictions by the Equilibrium and Coupled models, respectively, are found to be within a factor of 2 of the observations. Equilibrium model gave more consistent results as R^2 , normalized root-mean-square error (NRMSE) and bias varied less with the change of season as compared to the Coupled model results.

USEPA's air quality model, AERMOD, was used for studying dispersion and dry deposition of ammonia downwind of the selected two swine farms, viz., Barham farm and Moores farm. Measurements of ammonia flux from the waste lagoons and barns at Barham farm were made during spring and fall seasons. Moores farm measurements represented winter and summer seasons. Meteorological data on ambient temperature, wind speed, wind direction and RH from the farm sites were used to prepare meteorological input file for AERMOD. Cloud cover data was used from nearest North Carolina climate office's weather station. Two wind orientations were used for each farm to study change in deposition with wind orientation. Grass and crop surfaces were used separately to compare ammonia deposition on these two surfaces.

Dry deposition and meteorological data from Philips et al. (2004) were used to compare dry deposition velocity calculated by AERMOD. Modeled dry deposition values were smaller than the observed values, by a factor of 2 to 4 during day and up to 8 during night. These lower values are attributed to the lack of understanding of ammonia deposition from grass and crop surfaces. Observations show both deposition and emission occurring, depending on the compensation point at vegetation surface. AERMOD assumes compensation point to be zero.

Our model study of ammonia dispersion shows that ground level concentrations are very high near the farm and decrease rapidly as we move away from the farm. The rate of decrease in concentration with distance becomes smaller as we move further downwind of the farm. The decrease of concentration is faster under unstable conditions and the slowest under stable conditions. The rate of decrease in concentration with distance for near-neutral conditions lies somewhere between that for stable and unstable conditions. Ground level concentrations would be lower under unstable conditions for a given emission rate, but become higher than the near neutral conditions at certain distance downwind due to bi-Gaussian distribution of vertical distribution under unstable conditions. Dry deposition of ammonia up to 2500 m downwind of the farm is studied under different stability conditions and over crop and grass surfaces. Major contribution to deposition as percentage of total emission comes from the first 500 m from the farm where ground level concentrations are large. Deposition was the highest under stable conditions and the lowest under unstable conditions. Under stable conditions, more deposition occurred over the grass surface than over the crop surface with the exception of spring season where it was higher over the crop surface. Under unstable and near neutral conditions, deposition was higher over the crop surface for winter, summer and spring seasons. These differences between crop and grass surfaces were higher under stable conditions. Wind orientation can also make a difference on the downwind deposition depending on the layout of the source on the farm.

Further studies should be done by taking into account the possible effects of farm buildings. Study of the dry deposition of ammonia in the forest canopy downwind, if present, should also be studied. Better understanding of deposition parameterization and

soil and leaf chemistry is also needed to reduce the uncertainties involved in this study. It would also help in developing bi-directional flux model for NH_3 , which is necessary for complete understanding of ammonia deposition.

Appendix

Appendix 1. Measurement and Estimation of Ammonia Emissions From Lagoon-Atmosphere Interface using a Coupled Mass Transfer and Chemical Reactions Model, and an Equilibrium Model

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Ammonia has recently gained importance for its increasing atmospheric concentrations and its role in the formation of aerosols. The anaerobic lagoon and spray method, commonly used for waste storage and disposal in confined animal feeding operations (CAFO), is a significant source of ammonia emissions. An accurate emission model for ammonia from aqueous surfaces can help in the development of emission factors. Data collected from field measurements made at hog waste lagoons in south eastern North Carolina, using the flow through dynamic chamber technique, were used to evaluate the Coupled Mass Transfer and Chemical Reactions model and Equilibrium model developed by Aneja et al., (2001a). Sensitivity analysis shows that ammonia flux increases exponentially with lagoon temperature and pH, but a linear increase was observed with an increase in total ammoniacal nitrogen (TAN). Ammonia flux also shows a nonlinear increase with increasing wind speed. Observed ammonia fluxes were generally lower in the cold season than in the warm season when lagoon temperatures are higher. About 41% of the Equilibrium model predictions and 43% of the Coupled model predictions are found to be within a factor of two of the observed fluxes. Several model performance statistics were used to evaluate the performance of the two models against the observed flux data. These indicate that the simpler Equilibrium model does as well as the Coupled model. The possible effects of the “artificial” environment within the chamber, which is different from that in the ambient atmospheric conditions above the open lagoon surface, on the measured fluxes are also recognized.

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Appendix 2. Modeling studies of Ammonia Dispersion and Dry Deposition studies at some Hog farms in North Carolina.

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Modeling studies have been conducted on dispersion and dry deposition of ammonia taking one hog farm as a unit. Ammonia emissions used in this study were measured under our OPEN (Odor, Pathogens and Emissions of Nitrogen) project over waste lagoon and from the barns. Meteorological data was also collected at the farm site. Actual layout of barns and lagoons on the farms was used to simulate dry deposition downwind of the farm. Dry deposition velocity, dispersion and dry deposition of ammonia were studied over different seasons and under different stability conditions. Dry deposition velocities were highest under near neutral conditions and lowest under stable conditions. Highest deposition at short range occurs under night time stable conditions and lowest during daytime unstable conditions. Significant differences in deposition over crop and grass surfaces were observed under stable conditions.

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Appendix 3. Characterizing Ammonia Emissions from Swine Farms in Eastern North Carolina – Part I. Conventional Lagoon and Spray Technology for Waste Treatment

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Ammonia fluxes from waste treatment lagoons and barns at two conventional swine farms in eastern North Carolina were measured. The waste treatment lagoon data was analyzed to elucidate their temporal (seasonal and diurnal) variability, and to derive regression relationships between ammonia (NH₃) flux and lagoon temperature, pH and ammonium content of the lagoon, as well as the most relevant meteorological parameters. NH₃ fluxes were measured at various sampling locations on the lagoons by a flow-through dynamic chamber system interfaced to an environmentally controlled mobile laboratory. Two sets of open-path FTIR spectrometers were also used to measure NH₃ concentrations for estimating NH₃ emissions from the animal housing units (barns) at the conventional sites. Two different types of ventilation systems were employed at the two farms. Moore farm used fan ventilation, and Stokes farm used natural ventilation. NH₃ emissions from barns were estimated for two seasons (warm and cold) at Moore farm and one season for Stokes farm.

The early fall and winter season intensive measurement campaigns were conducted during September 9-October 11, 2002 (lagoon temperature ranged from 21.2 to 33.6 °C) and January 6-February 2, 2003 (lagoon temperature ranged from 1.7 to 12.0 °C), respectively. Significant differences in seasonal ammonia fluxes from the waste treatment lagoons were found at both the farms. Average NH₃ fluxes in the warm season (Stokes 2349.4 ± 986.4, Moore 1685.4 ± 516.4 μg-N m⁻² min⁻¹) were approximately an order of magnitude higher than those in the cold season (Stokes 152.7 ± 52.4, Moore 370 ± 147.1 μg-N m⁻² min⁻¹) at both of the farms. Typical diurnal variation of NH₃ flux with its maximum value in the afternoon was observed during both of the experimental periods. Exponentially increasing flux with increasing surface lagoon temperature was observed, and a simple linear regression relationship between logarithms of NH₃ flux and lagoon surface temperature (T_l) was obtained. Relationships between lagoon NH₃ flux and chemical parameters, such as pH, total Kjeldahl nitrogen (TKN) and total ammoniacal nitrogen (TAN) were also examined. The lagoon pH stayed within a relatively narrow range from 7.7 to 8.5 during fall and winter seasons. No significant correlation between

pH and lagoon NH₃ flux was found, while TKN and TAN concentration was negatively correlated with lagoon NH₃ flux. There was also a significant seasonal variability of TKN and TAN concentrations; relatively lower TKN and TAN concentrations were observed during the fall with higher NH₃ fluxes; and higher TKN and TAN concentrations were observed during the winter with lower NH₃ fluxes. This seasonal difference in TKN and TAN concentrations could also be attributed to different lagoon temperatures differences in fall and winter months. The difference (D) between air temperature and the lagoon surface temperature was also found to influence the NH₃ flux, especially when D>0. This hot air effect is included in the multiple regression model obtained in this study.

For barn emissions, there was little seasonal variation found at Moore farm, the average normalized NH₃ emissions were 1.05 and 0.89 kg-N/wk/1000 kg lw for October and January , respectively. At Stokes Farm, the average normalized NH₃ emissions were 0.25 kg-N/wk/1000 kg-lw.

The statistical multiple regression model and the barn emissions will be used to compare the emissions from potential environmental superior technologies in order to evaluate the effectiveness of each technology.

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Appendix 4. Characterizing Ammonia Emissions from Swine Farms in Eastern North Carolina-Part II. Potential Environmentally Superior Technologies for Waste Treatment

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The need for developing environmentally superior and sustainable solutions for managing the animal waste at commercial swine farms in eastern North Carolina has been recognized in recent years. The Program OPEN (Odor, Pathogens, and Emissions of Nitrogen) funded by North Carolina State University Animal and Poultry Waste Management Center (APWMC), was initiated and charged with the evaluation of potential environmentally superior technologies (ESTs) that have been developed and implemented at selected swine farms or facilities. It has demonstrated the effectiveness of a new paradigm for policy-relevant environmental research in North Carolina's animal waste management. This new paradigm is based on a commitment to improve scientific understanding associated with all aspects of environmental issues (movement of nitrogen from animal waste between air, water and soil media, odor and odorants, and disease-transmitting vector and airborne pathogens). The primary focus of this paper is on emissions of ammonia, or nitrogen associated with ammonia (NH₃-N), from some potential ESTs at swine facilities. During two-week long periods in two different seasons (warm and cold), NH₃ fluxes from water holding structures and NH₃ emissions from animal houses or barns were measured at six potential EST sites: (1) Barham Farm – in-ground ambient temperature anaerobic digester/energy recovery/greenhouse vegetable production system; (2) BOC # 93 farm- EKOKAN; (3) Carrolls farm- ISSUES-ABS; (4) Corbett # 1 farm; - Solids separation/gasification for energy and ash recovery centralized system (BEST) (5) Corbett # 2 Farm – solid separation/ reciprocating water technology (ReCip); (6) Vestal farm- ISSUES-RENEW.

The ESTs were compared with similar measurements from two conventional lagoon and spray technology (LST) farms (Moore Farm and Stokes Farm). A flow-through dynamic chamber system and two sets of open-path FTIR spectrometers measured continuously NH₃ fluxes from water holding structures and emissions from housing units at the EST and conventional LST sites. During the experimental periods, environmental parameters

such as air temperature, wind speed and direction, relative humidity, solar radiation, lagoon temperature, lagoon pH, and Total Kjeldahl Nitrogen (TKN) at all the experimental farm sites were measured. For comparing the emissions from water holding structures at ESTs with those from lagoons at conventional sites under similar environmental conditions, a statistical-observational model for lagoon NH₃ flux was developed, using a multiple linear regression analysis of 15-min averaged NH₃ flux data against the relevant environmental parameters measured at the two conventional farms, during two different seasons of year. Percentage reductions in NH₃ emissions from different components of the potential EST, as well as the whole farm were evaluated from the estimated emissions from water-holding structures, barns, etc., all normalized by the appropriate nitrogen excretion rate at the potential EST farm, as well as the appropriate conventional farm. This study showed that ammonia emissions were reduced by all but one potential EST for both experimental periods. However, based on our evaluation results and analysis, and available information in the scientific literature, the evaluated alternative technologies may require additional technical modifications to be qualified as unconditional EST relative to ammonia emissions reductions.

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Appendix 5. Characterizing Ammonia Emissions from Swine Farms in Eastern North Carolina-Part III. Reduction of NH₃ Emissions from Water-holding Structures at Two Environmentally Superior Technologies for Waste Treatment

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Program OPEN (Odor, Pathogens, and Emissions of Nitrogen) is an integrated study of the emissions of ammonia, odor and odorants and pathogens from potential environmentally superior technologies (ESTs) for swine facilities. This paper, as part of program OPEN, focuses on quantifying emissions of NH₃ from water-holding structures at two of the best ESTs and comparing them with projected emissions from two conventional lagoon and spray technology (LSTs). The evaluated ESTs are: (1) Super Soils at Goshen Ridge; (2) Environmental Technologies at Red Hill. The water-holding structures for these two ESTs contained no conventional anaerobic lagoon. A dynamic flow-through chamber was used to measure NH₃ fluxes from water-holding structures at the ESTs and conventional farms (LSTs). In order to compare the emissions from water-holding structures at ESTs with those from lagoons at conventional sites under similar conditions, a statistical-observational model for lagoon NH₃ was used. A mass balance approach was used to quantify the emissions. All emissions were normalized by nitrogen excretion rates. The percentage reduction was calculated for the two ESTs. Results showed substantial reductions of NH₃ emissions at both ESTs. Super Soils had reductions of 94.7% for the warm season and 99.0% for the cool season. Environmental technologies had slightly larger reductions of 99.4% and 99.98% for the cool and warm season, respectively.

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Appendix 6. Ammonia Emissions and Dry Deposition Studies at Some Hog Farms in North Carolina

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Experimental and modeling studies have been conducted on emissions, dispersion and dry deposition of ammonia taking one swine farm as a unit. Ammonia emission fluxes were measured during the years of 2002 to 2004. Measurements of ammonia flux were made at 11 swine facilities in North Carolina using a dynamic flow-through chamber system over the anaerobic waste treatment lagoons and other water holding structures, and each farm was measured during two 8-10 day periods representing warm and cold seasons. Barn emissions were also measured during those periods. Flux data was used to validate a process based Coupled mass transfer and chemical reaction model and an Equilibrium model developed by Aneja et al., (2001a) to better understand emission processes from lagoon surface. Several model performance statistics were used to evaluate the performance of the two models against the observed flux data. These indicate that the simpler Equilibrium model does as well as the Coupled model. Emission data from lagoon and barns is used to study short range downwind dispersion and dry deposition of ammonia from selected swine facilities using USEPA's AERMOD model.

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Appendix 7. Estimating ammonia emissions from lagoon-atmosphere interface by coupled mass transfer and chemical reaction model and WATER9 model\.

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Ammonia has recently gained importance for its increasing atmospheric concentrations and its role in the formation of aerosols. Anaerobic lagoon and spray method, commonly used for waste storage in confined animal feeding operations (CAFO), is a significant source of ammonia emissions. An emission model for ammonia from aqueous surface can help in the development of emission factors. Data collected from field measurements made at hog farm lagoons in south eastern North Carolina, using emission flux chamber, was used to validate the Coupled mass transfer and chemical reaction model and Equilibrium model developed by Aneja et al., (2001). Sensitivity analysis shows that ammonia flux increases exponentially with lagoon temperature and pH, but linear increase was observed with increase in total ammoniacal nitrogen (TAN). Ammonia flux shows a second degree increase with increasing wind speed. Model results of emissions based on the coupled mass transfer with chemical reactions agreed well with the measurements. However, the US EPA's WATER9 emissions model seems to predict greater ammonia emissions, especially at the higher wind speeds.

Aneja , V. P., Malik, B. P., Tong, Q., Kang, D., and Overton, J. H., "Measurement and modeling of ammonia emissions at waste treatment lagoon-atmospheric interface", Water, Air and Soil pollution: Focus 1, 177-188, 2001.

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