

DIFFERENTIAL OPTICAL ABSORPTION SPECTROSCOPY (DOAS)
MEASUREMENTS OF ATMOSPHERIC AMMONIA IN THE
MID-ULTRAVIOLET FROM A DAIRY:
CONCENTRATIONS, EMISSIONS,
AND MODELING

By

BRIAN PAUL RUMBURG

A dissertation submitted in partial fulfillment of
the requirements for the degree of

DOCTOR OF PHILOSOPHY

WASHINGTON STATE UNIVERSITY
Department of Civil & Environmental Engineering

MAY 2006

To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation
of BRIAN PAUL RUMBURG find it satisfactory and recommend that it be accepted.

Chair

ACKNOWLEDGMENTS

I would like to thank the members of my committee: Drs. George Mount, Brian Lamb, Hal Westberg, David Yonge, and Kristen Johnson for helping make this project possible and successful. I would like to thank Professor George Mount for having me as a student and for teaching me so very much. Thank you for your hard work to keep this project going and your continued belief in this project, it would not have been possible without you. To Professor Brian Lamb, your support and knowledge of flux measurements and modeling needs greatly improved the results of this project. Credit must be given to Professor Hal Westberg for having the forethought that NH_3 emissions in the U.S. needed to be measured. Thanks to Professor Dave Yonge for sharing your knowledge of wastewater systems and your support for the wastewater part of this project. The wastewater component of the project was integral to the study of dairy NH_3 emissions and abatement. I would like to thank Professors Kris Johnson and Ron Kincaid for sharing their knowledge of cows, the WSU dairy, and the dairy industry. The addition of the cow component to this project has helped make this a complete study of the dairy and how NH_3 emissions occur. I would like to thank all my committee members for supporting me and teaching me so much. Without all of your belief in this project it would not have been possible.

This project would also not have been successful without the hard work of many wonderful people who have helped in various ways. To Jenny Filipy, I am very grateful for all the hard work, we had a great time despite the trying conditions. I was very lucky to have you as a part of this project and in my life. To Manjit Neger, thank you so much for all your vital work on the lagoons. We had fun despite risking our lives. Thank you to Stacy Wetherelt for your work on the nitrogen balance of the dairy. Thank you to Steve Nelson for helping during the summer. Jay Bays, your work during the slurry experiment helped make that part of the project a success. Jeff Havig, thanks for helping get this project started and

lending your hard work and humor to this project. Thanks to Jack Chen for working on the modeling part of this project.

I would also like to thank everyone at the LAR for making the LAR an incredible place to learn and work. I cannot image a better learning and working environment. Special thanks to Dr. Dennis Finn for our talks about science and helping me decide to get my Ph.D..

Thanks to Lee Bamesburger for sharing your vast wealth of knowledge and all the technical help and the humor along the way. In my opinion, you deserve an honorary doctorate. Thanks to Gene Allwine for helping with the tracer equipment.

Thanks to John Swain, Ferris Forar and the staff of the WSU Knott Dairy Center for allowing us to make measurements and educating me about the dairy industry. Thanks to WSU Farm Services, especially Darral Manthey, for help with the aeration experiment and slurry experiment. A special thanks to Kurt Hutchinson and Gary Held from the college shop for their amazing engineering and machining skills. Thanks to Thelma Willett, Lola Gillespie, Kathy Cox, Vicki Ruddick, and Maureen Clausen for all your assistance.

Thanks to Dr. Jim Petersen for allowing me to be a part of the IGERT program. Thanks to the Washington Department of Ecology for funding part of this project. I would also like to thank Drs. Mike Katona and David McLean of the Department of Civil & Environmental Engineering for supporting this project.

This project has been a team effort, thanks to everyone who helped make it possible.

DIFFERENTIAL OPTICAL ABSORPTION SPECTROSCOPY (DOAS)
MEASUREMENTS OF ATMOSPHERIC AMMONIA IN THE
MID-ULTRAVIOLET FROM A DAIRY:
CONCENTRATIONS, EMISSIONS,
AND MODELING

Abstract

by Brian Paul Rumburg, Ph.D.
Washington State University
May 2006

Chair: George H. Mount

Atmospheric ammonia (NH_3) effects on the atmosphere, environment, and human health is not well understood due to a lack of information about ammonia's emissions, transport, and fate. Ammonia in the atmosphere reacts to form particulate matter below 2.5 microns in aerodynamic diameter ($\text{PM}_{2.5}$) which is regulated by the Environmental Protection Agency (EPA). The largest anthropogenic source of atmospheric NH_3 is animal excreta and dairy cows are the largest per animal emission source.

The objectives of this work were to measure and model NH_3 emissions from the Washington State University (WSU) dairy. Short-path differential optical absorption spectroscopy (DOAS) was used to measure NH_3 , and an area source tracer ratio technique was used to measure emission fluxes. Measurements were made from the housing area, waste lagoons, and fields undergoing sprinkler application. Emissions models were developed to understand the physical processes and transport of NH_3 . Housing emission fluxes for the summer averaged $8.1 \pm 5.2 \text{ mg cow}^{-1} \text{ s}^{-1}$ at 18° C average temperature. The housing model had an error of $\pm 30\%$ when compared to measured concentrations. Lagoon emission fluxes ranged

from $30 \mu\text{g m}^{-2} \text{s}^{-1}$ at an air temperature of 11°C to $150 \mu\text{g m}^{-2} \text{s}^{-1}$ at an air temperature of 27°C . The lagoon model had an error of $\pm 21\%$. An aeration experiment was conducted with commercial aerators and no changes in liquid or downwind NH_3 concentrations were detected during aeration. Slurry application emissions from the sprinkler were 18% of the slurry ammonia-N concentration. The initial tracer flux from the field was $47 \mu\text{g m}^{-2} \text{s}^{-1}$ and this decreased to $17 \mu\text{g m}^{-2} \text{s}^{-1}$ during the experiment due to slurry infiltration into the soil.

A total dairy emission model was developed for use with air quality models using the WSU algorithms. The total annual emissions are estimated to be $130 \text{ kg NH}_3 \text{ cow}^{-1} \text{ yr}^{-1}$, with 40 kg from housing, 55 kg from waste lagoons, and 34 kg from waste application. Annual emissions are in excellent agreement with annual N mass balance of the dairy. This is significantly larger than the EPA estimates which are based upon European data.

Table of Contents

Acknowledgments	iii
Abstract	v
List of Tables	xi
List of Figures	xiii
Dedication	xv
Chapter 1 Introduction	1
1.1 Abstract	1
Chapter 2 Literature Review	4
2.1 Background	5
2.1.1 Reactive Nitrogen	5
2.1.2 Ammonia	7
2.2 Ammonia Sources and Emissions	8
2.3 Natural Sources and Emissions of NH ₃	9
2.4 Anthropogenic Sources and Emissions	10
2.4.1 Domestic Animal Excretion	10
2.4.2 Fertilizer	10
2.4.3 Cropland	11
2.4.4 Fossil Fuel and Industry	11
2.4.5 Human Emissions	11
2.5 Chemistry	11
2.5.1 Ammonia Deposition	13
2.6 Dairy Housing Emissions	14
2.7 Lagoon Emissions	16
2.7.1 Lagoon Aeration	18
2.8 Slurry Application	20
2.9 Ammonia Emissions Modeling and Estimates	23
Chapter 3 Methodology	26
3.1 Differential Optical Absorption Spectroscopy	26
3.1.1 Instrumentation	29
3.1.2 Data Collection	31
3.1.3 Data Analysis	33
3.2 Area Source Tracer Techniques	34
3.3 WSU Dairy	37
3.3.1 Nitrogen Mass Balance: A Test For Measured Total Emissions	39

Chapter 4	Housing Emissions	42
4.1	Abstract	43
4.2	Introduction	44
4.3	Experimental	46
4.3.1	Dairy Information	46
4.3.2	Nitrogen Mass Balance	48
4.3.3	Air Analysis	50
4.3.4	Sulfur Hexafluoride Tracer Ratio Technique	51
4.3.5	Emissions Model	53
4.4	Results and Discussion	57
4.4.1	Concentration Measurements	57
4.4.2	Tracer Ratio Experiments	59
4.4.3	Emissions Model	62
4.4.4	Modeling Sensitivity Analysis	62
4.4.5	Annual Emissions	65
4.5	Approximate Error Analysis	65
4.6	Conclusions	67
Chapter 5	Lagoon Emissions	69
5.1	Abstract	70
5.2	Introduction	70
5.3	Experimental	73
5.3.1	Dairy Information	73
5.3.2	Liquid Analysis	74
5.3.3	Air Analysis	74
5.3.4	Sulfur Hexafluoride Tracer Ratio Technique	76
5.3.5	Theoretical Model	78
5.4	Results and Discussion	82
5.4.1	Tracer Experiments	82
5.4.2	Emission Algorithm	83
5.4.3	Annual Emissions	84
5.4.4	Modeling Sensitivity Analysis	88
5.5	Lagoon Emission Rate Error Analysis	89
5.6	Conclusions	91
Chapter 6	Aeration Experiment	92
6.1	Abstract	93
6.2	Introduction	93
6.3	Methods	97
6.3.1	Knott Dairy Center	97
6.3.2	Aerators	99
6.3.3	Water Analysis	101
6.3.4	Air Analysis	101
6.3.5	Experimental	102
6.4	Results and Discussion	104

6.4.1	Water Results	104
6.4.2	Air Results	105
6.5	Conclusions	109
Chapter 7 Slurry Application Emissions		112
7.1	Abstract	113
7.2	Introduction	113
7.3	Experimental	116
7.3.1	Dairy Information	117
7.3.2	Liquid Analysis	118
7.3.3	Soil Analysis	118
7.3.4	Air Analysis	119
7.3.5	Sulfur Hexafluoride Tracer Technique	119
7.4	Emissions Modeling	121
7.4.1	Empirical Model	121
7.4.2	Theoretical Model	121
7.4.3	Water content at the soil surface	123
7.4.4	Soil surface temperature	123
7.5	Results and Discussion	124
7.5.1	Slurry Sprinkler Volatilization	124
7.5.2	Soil N Results	124
7.5.3	Air Results	125
7.6	Empirical Model	127
7.6.1	Theoretical Model	129
7.6.2	Total Emissions	130
7.7	Uncertainty Analysis	131
7.8	Conclusions	132
Chapter 8 Ammonia Dairy Emissions Model		134
8.1	Abstract	135
8.2	Introduction	135
8.3	Model Development	138
8.3.1	WSU Dairy Information	139
8.3.2	Milking Cow Housing Emissions Module	139
8.3.3	Waste Storage Emissions Module	141
8.3.4	Waste Application Module	143
8.4	Results	144
8.4.1	Housing Emissions	144
8.4.2	Lagoon Emissions Module	145
8.4.3	Waste Application Emissions	147
8.5	Conclusions	149

Chapter 9	Conclusions and Future Work	151
9.1	Conclusions	151
9.1.1	Housing Emissions	152
9.1.2	Lagoon Emissions	153
9.1.3	Waste Application Emissions	155
9.1.4	WSU Dairy Emissions Model	156
9.2	Future Work	158
9.2.1	Washington State Dairy Emissions	158
9.2.2	WSU Dairy Ammonia Emissions Reduction	160
Chapter 10	Bibliography	162

List of Tables

2.1	Annual estimated NH ₃ emissions from the referenced sources listed below. All units are Tg N yr ⁻¹	8
3.1	Suggested variables for calculating σ_z based upon stability from Busse and Zimmerman, (1973).	36
3.2	Nitrogen mass balance for the milking cows and waste treatment system of the WSU Knott Dairy Center. Nitrogen imports are additions to the milking cow stall area or the waste lagoon system and exports are subtractions from the stalls or lagoon system not accounting for volatilization.	39
4.1	Nitrogen mass balance for the milking cows and waste treatment system of the WSU Knott Dairy Center. Nitrogen imports are additions to the milking cow stall area or the waste lagoon system and exports are subtractions from the stalls or lagoon system not accounting for volatilization.	49
4.2	Housing emissions sensitivity analysis of measured NH ₃ concentrations versus downwind modeled concentrations for 110 half-hour average time periods. Sensitivity statistics: mean bias (MB), normalized mean bias (NMB), normalized mean error (NME) and average flux. Average model flux and standard deviation for the time periods.	64
5.1	Waste storage model sensitivity analysis for downwind lagoon concentrations from 2000 to 2003. Base case using measured air temperature, pH of 7.8, and ammonia-N concentration of 660 mg L ⁻¹ above 10° C and 530 mg L ⁻¹ below. Sensitivity statistics: mean bias (MB), normalized mean bias (NMB), and normalized mean error (NME).	90
7.1	Slurry experiment field bottle concentrations of ammonia-N and TKN along with depth of slurry in the bottle. Location is direction relative to sprinkler and distance from sprinkler in m. Only bottles with measurable amounts of slurry are shown, <i>a</i> denotes bottles flooded when the sprinkler turned off. . .	125
8.1	Milking cow housing from USDA (2003) survey of manure handling methods. Majority percent represents where the majority of the cows at each dairy are housed, percent used represents dairies that have multiple housing types for the cows.	140
8.2	WSU dairy information for housing emissions module.	141
8.3	National survey results of waste storage practices in the U.S. . The majority percent column is how the majority of the waste on the farm is stored and the percent used column represents the usage of different types of waste storage (USDA, 2003).	142

8.4	Maximum dairy waste storage times in the U.S.. (USDA, 2003).	142
8.5	USDA survey of application types used. Numbers do not add up to 100% due to some dairies using multiple methods of waste application.	144
8.6	Housing emissions model sensitivity analysis. Base case conditions, milk production 41 kg day^{-1} , crude protein (CP) equals 19%, $\text{pH} = 7.8$, $h_m = 5.8 \times 10^{-4}$, ambient air temperature, and a wind speed threshold where there is no transfer to the bulk atmosphere of 1 m^{-1}	146
8.7	Lagoon emissions model sensitivity analysis. Base case conditions are 4 lagoons with 2 used as storage during part of the year, TAN concentration of 660 mg L^{-1} for temperatures above 10° C and 530 mg L^{-1} for temperature below that, $\text{pH} = 7.8$, $h_m = 0.00058$, ambient air temperature, wind speed threshold below which there is no mass transfer to the atmosphere of 1.5 m s^{-1} .	148
9.1	Annual NH_3 emissions from the WSU dairy by source. Housing emissions uncertainties are based upon comparison to measurements and are 30% and lagoon emissions are also based up measurements and the uncertainty is 20%, waste application errors are based upon measurement error and are 10% for the sprinkler and 50% for the field emissions. Nitrogen mass balance numbers are based upon measurements and an estimated uncertainty of 20%. The waste application sprinkler emissions are based upon the mass balance so the numbers are the same. Mass balance field calculations were not possible. . .	157

List of Figures

3.1	WSU NH ₃ instrument. The Xe light source at the left illuminating the folding mirror used to direct the beam to the telescope on the right. The mirror used to direct the light to the spectrograph is to the right of the folding mirror. The spectrograph is the black instrument above and to the right of the light source and the entrance slit is above the light source.	30
4.1	WSU Knott Dairy Center milking stalls contour map. Measurements made at the north milking stalls, black rectangle signifies the instrument position and circle signifies the retroreflector mirror position and the dashed line is the measurement path.	47
4.2	North milking stalls with spectrograph and light source in the trailer, retroreflectors on the right, tracer gas syringe samplers on the stands, during tracer experiment.	48
4.3	Ammonia concentrations (upper panel) averaged over approximately 2 minutes and wind speed and direction (lower panel) averaged over 10 minutes showing the the relationship between wind speed and direction and NH ₃ concentrations.	58
4.4	Ammonia concentrations (ppbv) for July 23, 2003. Measurements averaged every minute demonstrate the turbulence in the stalls.	59
4.5	Point source tracer experiment, NH ₃ and SF ₆ concentrations on the top panel and wind speed and NH ₃ flux on the bottom panel.	61
4.6	Half-hour averaged measured and modeled NH ₃ concentrations (ppbv) from the milking stalls from 2001 to 2004. Solid line is the 1:1 line.	63
4.7	Daily model predicted NH ₃ emissions from the milking stalls (top panel) and daily average temperature (bottom panel). Wind speed and direction measured near the NH ₃ path and the SF ₆ syringe samplers.	66
5.1	WSU Knott Dairy Center countour map. Arrows represent slurry flow between lagoons and stalls and solids separator. Instrument position and retroreflector mirror location designating the instrument path (dashed line) is shown to the left of lagoon 2. Elevation contours are in m. Wind typically is out of the west.	75
5.2	Top panel shows lagoon 2 ammonia-N concentrations (mg L ⁻¹) as a function of time with the dashed line showing the date waste from lagoons 3 and 4 were added diluting the lagoon concentration. Bottom panel shows lagoon ammonia-N concentration as a function of temperature (circles on left axis) and theoretical flux based upon temperature (squares on right axis).	80

5.3	Ammonia concentration (solid line, left axis) 50 m downwind of lagoon 2 measured approximately every second and wind direction (dashed line, right axis). Bars on right axis mark optimal wind direction.	82
5.4	Theoretical model of downwind NH ₃ concentrations (ppbv). Top panel shows model using lagoon temperature in the model and the bottom panel shows using the air temperature.	85
5.5	Theoretical lagoon model daily NH ₃ flux (upper panel) for 2001 and average daily temperature. At day 240 lagoons 3 and 4 were emptied and filled again about day 310.	87
6.1	Contour map of the Washington State University Knott Dairy. Wastewater lagoons are shown in dark gray and buildings in light gray. Arrows indicate wastewater piping system. Wastewater from lagoon 2 is used to flush the pits at the milking cow stalls when the stalls are scraped. Solids are removed at the solids separator and further removed via gravity settling in lagoon 1. Typical west winds blow across lagoon 2 to the ammonia instrumentation.	98
6.2	Lagoon 2 wastewater sampling sites (boxes) and position of CirCulators TM (circles) and instrument set up downwind with the instrument path denoted by the dashed line.	100
6.3	Lagoon 2 wastewater average, upper and lower NH ₃ -N and TKN concentrations without the dilution correction (upper panel) and with dilution correction (lower panel). TKN analysis error averaged 2.1%. NH ₃ analysis error averaged 3.8%.	106
6.4	Lagoon 2 wastewater total solids (upper panel) and volatile solids (lower panel) using a dilution factor of 1.13 times all samples taken after day 210. Whiskers are one standard deviation from the depth average.	107
6.5	Atmospheric NH ₃ concentrations downwind of lagoon 2 before, during and after the aeration experiment. Concentrations sorted for wind direction within 15° of directly over lagoon to instrument path and wind direction standard deviation of less than 15°.	108
6.6	Atmospheric NH ₃ concentrations downwind of lagoon 2 before, during and after the aeration experiment. Gray marker in box is average NH ₃ concentration, box is 25 th and 75 th percentiles, whiskers are 10 th and 90 th percentiles. Concentrations sorted for wind direction within 15° of directly over lagoon to instrument path and wind direction standard deviation of less than 15°.	110
7.1	Sprinkler applying waste to the grass field.	117
7.2	Soil ammonia-N (top panel) and NO ₃ ⁻ -N (bottom panel) concentrations with direction and distance in meters from the sprinkler. Horizontal lines indicate average background levels.	126
7.3	NH ₃ concentrations (upper panel) and wind speed and wind direction with horizontal bars showing wind directions towards instrument path (lower panel) during the slurry experiment.	128

7.4 Slurry experiment half hour measured concentrations and emiprical fit modeled concentrations and theoretical modeled concentrations. Empirical model not run for low wind conditions. 129

DEDICATION

This thesis is dedicated to my mother who taught me the value of a good education,
without your support this thesis would not have been possible.

Chapter 1

Introduction

1.1 Abstract

Ammonia (NH_3) emissions and the impact of atmospheric NH_3 on human health and the environment in the United States are not well understood due in part to a lack of measurement data from the major anthropogenic sources - waste from domesticated animals. The measurement of atmospheric NH_3 is difficult since it adheres to instrument inlet walls creating measurement artifacts. The United States Environmental Protection Agency (EPA) established a new standard for particulate matter with an aerodynamic diameter less than 2.5 microns ($\text{PM}_{2.5}$) in 1997, NH_3 reacts with nitrate and sulfate species in the atmosphere to form $\text{PM}_{2.5}$. The passage of the $\text{PM}_{2.5}$ standard has led to increased interest in NH_3 emissions. Current U.S. emission estimates are based upon European measurements where farming practices and regulations are different from the U.S., leading to large errors in estimated NH_3 emissions. Most current emission estimates are also crude annual estimates based upon a few measurements and do not reflect the influence of meteorology on emissions. Ammonia emissions vary seasonally due to the temperature dependence of the volatilization rate and the production of NH_3 from the biological breakdown of organic N in animal waste. Emissions vary with farming practices and housing methods. Cows produce the largest fraction of NH_3 globally, and of these, dairy cows have the largest per animal emissions due to their consumption of large amounts of protein for milk production.

The objective of the Washington State University (WSU) Dairy Ammonia Emissions Project was to determine the atmospheric fluxes of NH_3 from the milking cow emission sources at the WSU Knott Dairy Center and to develop time resolved and meteorologically dependent emission algorithms for use in atmospheric models. A short-path differential optical absorption spectroscopy (DOAS) method was employed to measure the concentration

of NH_3 from the dairy milking stalls, waste lagoons, and during slurry application to grass fields. An area source tracer ratio technique was used to calculate emission fluxes. Theoretical models of the chemical and physical reactions of N related to NH_3 emissions were developed. Tracer ratio data was also used to calibrate a Gaussian plume dispersion model for times when tracer ratio experiments were not being conducted. The theoretical emissions model and the dispersion model were compared to measured concentrations. An analysis of model sensitivity was performed to evaluate the relative change in model output to different input values. Volatile organic compounds that contribute to the odors emitted from the dairy were also measured. Concentrations and emissions fluxes for certain compounds were reported (Filipy et al., 2006).

A total dairy farm emissions model was developed for the housing, waste lagoons, and waste application to run in statewide air quality models. A model input sensitivity analysis was performed and average daily, peak daily, and annual emissions were compared.

This thesis discusses the following: Chapter Two is a literature review examining the impact of NH_3 emissions on the atmosphere and the environment. The DOAS method and the tracer technique along with information about the WSU dairy is described in Chapter Three. Chapter Four is a manuscript describing the emissions from milking cow housing entitled Measurement and Modeling of Atmospheric Flux of Ammonia from Dairy Milking Cow Housing. Chapter Five is a submitted manuscript about the emissions of NH_3 from the waste lagoon entitled Atmospheric Flux of Ammonia from an Anaerobic Dairy Waste Lagoon. A published paper concerning the results of an experiment looking at aeration of the dairy lagoon entitled Atmospheric Flux of Ammonia from an Anaerobic Dairy Waste Lagoon is presented in Chapter Six. Chapter Seven is a submitted manuscript about the emissions from the slurry application to grass fields using a sprinkler entitled Atmospheric Flux of Ammonia from Sprinkler Application of Dairy Waste. Chapter Eight is a manuscript describing the development of an emissions model for dairies entitled A Dairy Ammonia Emissions Model for Milking Cow Housing, Waste Lagoons and Sprinkler Application. Chapter Nine is the

conclusions and suggestions for future work.

Chapter 2

Literature Review

Ammonia (NH_3) emissions and the impact of atmospheric NH_3 on human health and the environment in the United States are not well understood due in part to a lack of measurement data from the major anthropogenic sources - waste from domesticated animals. The measurement of atmospheric NH_3 is difficult since it adheres to instrument inlet walls creating measurement artifacts. The United States Environmental Protection Agency (EPA) established a new standard for particulate matter with an aerodynamic diameter less than 2.5 microns ($\text{PM}_{2.5}$) in 1997, and NH_3 reacts with nitrate and sulfate species in the atmosphere to form $\text{PM}_{2.5}$. The passage of the $\text{PM}_{2.5}$ standard has led to increased interest in NH_3 emissions. Current U.S. emission estimates are based upon European measurements where farming practices and regulations are different from the U.S., leading to large errors in predicted NH_3 emissions. Most current emission estimates are also crude annual estimates based upon a few measurements and do not reflect the important influence of meteorology on emissions. Ammonia emissions vary seasonally due to the temperature dependence of the volatilization rate and the production of NH_3 from the biological breakdown of organic N in animal waste. Emissions vary with farming practices and housing methods. Cows produce the largest fraction of NH_3 globally, and of these, dairy cows have the largest per animal emissions due to their consumption of large amounts of protein for milk production.

The objective of the Washington State University (WSU) Dairy Ammonia Emissions Project was to determine the atmospheric fluxes of NH_3 from the milking cow emission sources at the WSU Knott Dairy Center and to develop high time resolved and meteorologically dependent emission algorithms for use in atmospheric models. A short-path differential optical absorption spectroscopy (DOAS) method was employed to measure the concentration of NH_3 from the dairy milking stalls, waste lagoons, and during slurry application to grass fields. An area source tracer ratio technique was used to calculate emission fluxes.

Theoretical models of the chemical and physical reactions of N related to NH₃ emissions were developed. Tracer ratio data was also used to calibrate a Gaussian plume dispersion model for times when tracer ratio experiments were not being conducted. The theoretical emissions model and the dispersion model were compared to measured concentrations. An analysis of model sensitivity was performed to evaluate the relative change in model output to different input values.

A total dairy farm emissions model was developed for the housing, waste lagoons, and waste application to run in state wide air quality models. A model input sensitivity analysis was performed and average daily, peak daily and annual emissions were compared.

2.1 Background

2.1.1 Reactive Nitrogen

The role of atmospheric NH₃ in the atmosphere and environment is very complex due to its vital role in the life cycle of the planet and the many reactions that can take place both in the atmosphere and the environment where it deposits. There are many uncertainties in the the role NH₃ plays both in the atmosphere and the environment due to a lack of measurement data and anthropogenic changes to the N and C cycles of the planet. Since NH₃ can be transformed into many other forms of N that is available for plant and animal life it is important to understand not only the NH₃ cycle but the N cycle of the planet. Nitrogen is often the limiting nutrient in many organisms so an excess of N is very important to the balance of life on the planet.

Nitrogen is one of the molecules that make up proteins required by all life on this planet. It is estimated that there is approximately 5 Pg (1 Pg = 10¹⁵ g) of N at the surface of the planet, but less than 2% is in a usable form for most organisms (Mackenzie, 1998). Approximately 20% of the global N is in sedimentary rock and approximately 78% exists as triple-bonded N₂ in the atmosphere. The N in rock is not readily available to organisms

so the atmosphere is the most important reservoir. Only a few organisms can convert the atmospheric N_2 into a reactive nitrogen (Nr), defined as N bonded to carbon, oxygen or hydrogen, and is the form usable by most organisms. The only two natural processes to create Nr are biological N fixation (BNF) and lightning. Since Nr is required for life and only a few organisms can fix N_2 to Nr there has been a natural limit to the growth of life on the planet.

Terrestrial natural BNF is estimated to produce between 90 and 130 Tg ($1 \text{ Tg} = 10^{12} \text{ g}$) of Nr to the environment each year (Galloway, 1998). Most of the BNF is formed by microorganisms living symbiotically with plants like legumes. Most of the terrestrial BNF is used by the biota near the source and only about 10% is emitted into the atmosphere (Galloway, 1998). It is estimated that prior to industrialization the rate of BNF and denitrification were about equal (Delwiche, 1970). The exchange of BNF between the marine environment and terrestrial environments is thought to have been very small due to the balance of nitrification and denitrification on land and in the oceans (Galloway et al., 1995). The terrestrial input of Nr to the oceans from runoff is estimated to be about 35 Tg N yr^{-1} (Galloway et al., 1995). Marine environments are estimated to produce about $40\text{-}200 \text{ Tg N yr}^{-1}$ (Galloway, 1998). The transport of Nr from the oceans to the terrestrial ecosystem is through fisheries and the transfer of NH_3 volatilizing and depositing on the land is thought to be small (Galloway, 1998).

In the early 1900s BNF was discovered and soon after the Haber-Bosch process of synthesizing NH_3 from hydrogen and nitrogen was discovered and that made it possible for humans to produce Nr for fertilizer. In about the 1950s the production of Nr via the Haber-Bosch process increased dramatically and that preceded a large increase in human population (Galloway and Cowling, 2002). By the mid-1990s human activity is estimated to be producing about 140 Tg N yr^{-1} which is up significantly from the 1970s when the estimate was only 70 Tg N yr^{-1} (Galloway et al., 1995). All of the impacts of current anthropogenic Nr emissions are not known. How an increasing need for Nr to keep pace with a growing human

population will affect the environment in the future is highly uncertain.

The Nr cycle is complicated due to the fact that there are multiple reaction pathways and most ecosystems are adapted to the natural Nr levels. Changing the Nr levels changes the dynamics of the plant species, herbivores and predators (Vitousek, et al., 1997). Excess Nr can also lead to soil nutrient losses and soil and aquatic acidification which can ultimately lead to decreases in soil fertility (Vitousek et al., 1997). Due to the importance of the changes humans are making to the Nr cycle of the planet it is important to understand the ultimate effects of the alteration of the Nr cycle. Ammonia is one of the important Nr species, due to its volatility and environmental impacts. Understanding NH_3 emissions and cycling will help in the understanding of the Nr cycle.

2.1.2 Ammonia

There are large uncertainties in Nr emissions and NH_3 is no exception. Ammonia is difficult to measure since it adheres to instrument inlet walls. Ammonia is the most abundant basic gas in the atmosphere and has many atmospheric reaction pathways depending upon what is available for it to react with. Ammonia will react with nitrate and sulfate species to form ammonium nitrate and sulfate aerosols. These fine aerosols are regulated as part of the U.S. Environmental Protection Agency (EPA) $\text{PM}_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 microns) criteria pollutants. $\text{PM}_{2.5}$ has been shown to cause health effects in humans, but it is not known at this time whether it is the mass loading or the chemical composition (Schwartz, 1994). Aerosols also impact global radiative transfer and visibility (Seinfeld and Pandis, 1996). When NH_3 reacts with OH it will produce the NH_2 radical which will then react to form N_2O which is a greenhouse gas. The deposition of NH_3 causes eutrophication in sensitive aquatic and terrestrial environments and potentially affects acidification of soils and aquatic environments (Vitousek et al., 1997)

Table 2.1: Annual estimated NH₃ emissions from the referenced sources listed below. All units are Tg N yr⁻¹.

	Dentener (1995)	Bouwman (1997)	Schlesinger (1992)	Olivier (1998)
Wild Animals	2.5	0.1	-	0.1
Vegetation	5.1	2.4	10	2.4
Ocean	7.0	8.2	13	8.2
Total Natural	14.6	16.8	23	10.7
Cattle & Buffaloes	14.2	14.0	19.9	12.9
Pigs	2.8	3.4	2.0	3.4
Horses	1.2	0.5	1.8	-
Sheep/Goats	2.5	1.5	4.1	-
Poultry	1.3	1.9	2.4	-
Other Animals	-	-	-	5.3
Fertilizer	6.4	9.0	8.5	9.0
Biomass Burning	2.0	5.7	5.0	5.9
Cropland	-	3.6	-	3.6
Fossil Fuel & Industry	-	0.3	2.2	0.3
Humans	-	2.6	4	2.6
Total Anthropogenic	30.4	36.8	49.9	43.0
Total Emissions	45	53.6	75	53.7

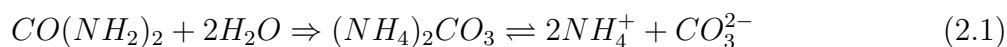
2.2 Ammonia Sources and Emissions

Global estimated NH₃ emissions are listed in Table 2.1. Bouwman et al., 1997 estimated the uncertainty in their global NH₃ emissions at $\pm 25\%$. Natural emissions are roughly half of estimated anthropogenic emissions. Most of the studies of NH₃ emissions have come from Europe where the close proximity of urban areas and agriculture has resulted in more public interest in NH₃ and other associated odorous compounds from livestock operations. Nitrogen deposition in Europe is reported to be much higher than in the U.S., so there is a scientific basis for the interest and some European countries have N emissions regulations (Bussink and Oenema, 1998).

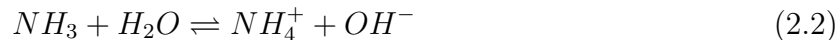
2.3 Natural Sources and Emissions of NH₃

As shown in Table 2.1 most of the natural emissions of NH₃ are from the oceans due to the volatilization of NH₃ from seawater. The flux depends upon the oceanic and atmospheric NH₃ concentrations, water salinity, and temperature (Bouwman et al., 1997). Soils emit NH₃ from organisms involved in the breakdown of organic matter. Many of these organisms give off NH₃ or NH₄⁺ directly, but emissions are highly variable due to the depth of emissions in the soil and the vegetative cover around the emissions where NH₃ might deposit (Bouwman et al., 1997). Vegetation can also be a source of NH₃ depending upon the atmospheric concentration (Langford and Fehsenfeld, 1992).

Excreta from animals is a minor natural source but a major anthropogenic source of NH₃ into the atmosphere. There are two reaction pathways for the formation of NH₃. The first is the reaction of urea in urine with urease in the manure or soil to form liquid ammonia-N (NH₃ and NH₄⁺) as described below, and the second is the microbiological anaerobic breakdown of organic N. Aqueous NH₃ is volatile, so depending upon the conditions, NH₃ in solution can volatilize. The hydrolysis of urea in urine with urease in the feces or soil is shown by the following reaction.



Ammonium will be in equilibrium with NH₃ depending upon the pH of the solution. The reaction is shown below.



The concentration of NH₃ in the solution is temperature and pH dependent; NH₃ increases with increasing temperature and pH. Atmospheric volatilization of NH₃ will occur when the surrounding air has a lower concentration than the solution.

Natural animal emissions are not as high as domesticated emissions because of the lower

animal density and location of excretions. The lower animal density means that most of the urine will react with urease in the soil instead of manure. The soil urease concentration is lower than for manure so the conversion of urea to NH_3 is slower for urine deposited in natural areas versus areas of high animal density. This lower urease concentration also allows more time for plant uptake of the N_r in the urine. Urine deposited in areas with a vegetative canopy, if it does react to form NH_3 , is more likely not to travel far due to NH_3 deposition.

2.4 Anthropogenic Sources and Emissions

2.4.1 Domestic Animal Excretion

The dominant source of global NH_3 is excreta from domestic animals (Table 2.1). Emissions are the result of urea in the urine and urease in the soil and manure as shown in Reaction 4.1. The high density of animals results in a greater likelihood for urea to react with urease. In addition to the reaction of urea and urease, NH_3 can be formed from the microbiological anaerobic breakdown of organic N in the urine and manure. Domestic animal waste storage is used in some farming circumstances to treat waste or store it prior to disposal, especially in the U.S..

Increasing human population has led to more domesticated animals to feed more people and that has led to increased NH_3 emissions; this trend is expected to continue into the future (Vitousek et al., 1997).

2.4.2 Fertilizer

Synthetic fertilizer application is another anthropogenic source of NH_3 emissions that is not well understood. The type of fertilizer applied affects emissions as well as do the soil properties such as soil pH, water content, porosity, and other factors influence emissions. Meteorology factors like wind speed, temperature and precipitation also affect NH_3 emission rates (Bouwman et al., 1997). Due to the many factors influencing emissions and lack of emissions data there are large uncertainties in the emissions.

2.4.3 Cropland

Crop emissions of NH_3 are similar to natural vegetation emissions and are dependent upon the concentration of NH_3 in the plant. Cropland is also a source when vegetative burning occurs to clear cropland or when crop residue is burned.

2.4.4 Fossil Fuel and Industry

Incomplete combustion of fossil fuels produces atmospheric NH_3 emissions. The emission rate is highly uncertain. The use of engine emission controls to reduce NO and NO_2 emissions has increased NH_3 emission rates for cars with emission controls (Bouwman et al., 1997). The combustion of coal and natural gas also releases NH_3 to the atmosphere. Industrial releases of NH_3 also occur due to the production of fertilizer and explosives (Bouwman et al., 1997).

2.4.5 Human Emissions

Direct human emissions are from waste and waste treatment systems, breath, and sweat. Emissions from waste treatment systems are the result of anaerobic degradation and are not well studied and most likely highly variable due to differences in waste treatment systems (Bouwman et al., 1997).

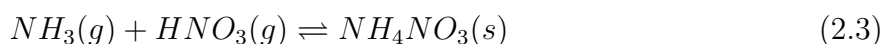
2.5 Chemistry

Since, ammonia is highly reactive in the atmosphere, it will react with water to form the ammonium ion NH_4^+ . Being the most abundant basic gas it will also react quickly with acidic species. Recent interest in NH_3 is in part due to the fact that NH_3 will react with sulfate or nitrate species to form fine aerosols that are a human health concern and are regulated by the U.S. EPA.

Ammonia will react with sulfuric acid in the atmosphere to form various sulfate aerosols. For a simple system of H_2SO_4 , NH_3 , and water, the NH_3 and H_2SO_4 will first react to form

the aerosol $\text{NH}_4\text{H}_2\text{SO}_4(\text{s})$ as long as there is sufficient water in the atmosphere (Seinfeld and Pandis, 1998). Once atmospheric water is consumed, $(\text{NH}_4^+)_3\text{H}(\text{SO}_4)_2(\text{s})$ and $(\text{NH}_4^+)_2\text{SO}_4(\text{s})$ will form and $\text{NH}_4\text{H}_2\text{SO}_4(\text{s})$ will be depleted. The reaction of NH_3 with sulfuric acid will continue until either all the sulfuric acid is consumed or all of the NH_3 is consumed.

The reaction of NH_3 with sulfate is the favored reaction, but if there is an excess of NH_3 then it will react with nitric acid gases in the atmosphere to form ammonium nitrate which is also a fine aerosol:



If the relative humidity is high enough, the ammonium nitrate may also be an aqueous solution of NH_4^+ and NO_3^- . See Seinfeld and Pandis (1998) for a complete description of the nitric acid and NH_3 chemistry.

In an atmosphere with both sulfuric and nitric acids there must be two times the amount of NH_3 as sulfuric acid before the reactions between NH_3 and nitric acid will take place. Since NH_3 neutralizes the sulfuric and nitric acids in the atmosphere, if there is not enough NH_3 in the atmosphere, the aerosol phase will be acidic. If there is sufficient NH_3 to react with and neutralize the sulfuric acid, then the NH_3 will react and form ammonium nitrate. See Seinfeld and Pandis (1996) for a more complete description of the ammonia, sulfuric acid and nitric acid chemistry.

In addition to the potential for human health impacts by $\text{PM}_{2.5}$, sulfate aerosols play a role in anthropogenic global climate change. Sulfate aerosols backscatter incoming solar radiation and they act as cloud condensation nuclei to increase the albedo of the planet. The net effect is most likely negative but the uncertainty in the effect is large (Seinfeld and Pandis, 1998).

Ammonia will also react with the hydroxyl radical as shown in Equation 2.4, but this reaction is slow and the above reactions are more likely. The following reactions show the process:



If the NH_2 radical reacts with NO_2 , nitrous oxide will be produced.



The important aspect Equation 2.5 is that N_2O is a byproduct and that N_2O is a very potent greenhouse gas. Nitrous oxide has a large energy absorption capacity per molecule and has a long atmospheric lifetime (Seinfeld and Pandis, 1998).

2.5.1 Ammonia Deposition

Since NH_3 is emitted primarily from ground sources and it adheres to surfaces readily, its atmospheric transport is limited. The primary removal of NH_3 and NH_4^+ is by dry and wet deposition. Ammonia has an estimated lifetime in the atmosphere of one to five days (Langford and Fehsenfeld, 1992), and if it reacts with water to form NH_4^+ then its lifetime can be up to ten days (Warnek, 1988). Ecosystems can be acidified if the NH_3 reacts with sulfuric acid and forms ammonium sulfate. The deposition of 1 mol of ammonium sulfate will result in 4 mol of acid into the environment by nitrification (Van Breemen et al., 1982). Fowler et al., 1998 found that the greatest deposition occurred close to the source, but it was only 3 to 10% of the total emissions. Due to the fast deposition of NH_3 , coarse grid (20 km) modeling of NH_3 deposition does not show the same variability as 5 km grid modeling (Sutton et al., 1998). It was found by Sutton et al. (1998) that it is important to account for the surface-atmosphere exchange instead of using simple deposition velocities to get NH_3 budgets.

More research into NH_3 emissions and fate in the atmosphere and the environment is needed to determine the ultimate impact of NH_3 emissions. Since local emissions are not known it is difficult to model the impacts of NH_3 emissions.

2.6 Dairy Housing Emissions

Milking cows have the largest per animal emissions of NH_3 due to the large amount of energy and protein required for milk production. Animal waste contains N in different forms and depending on the form and conditions can react to form NH_3 that can volatilize into the atmosphere. The fastest reaction pathway for the formation of NH_3 is from the N in the urine. Urinary urea-N (UUN) will react with the enzyme urease in the soil or in manure to form aqueous ammonium which can disassociate to form NH_3 as shown in Equations 4.1 and 2.2.

The liquid NH_4^+ and NH_3 will be in equilibrium depending upon the pH of the urine puddle. Ammonia can volatilize depending upon the pH, temperature, and mass transfer to the free atmosphere. Organic N in the manure can also react to form NH_3 under anaerobic conditions but this reaction is slow and not likely from housing areas that are regularly cleaned.

Cassel et al., 2005a measured NH_3 fluxes from open-lot dairies in California in the winter using bubblers with 50 cm Teflon tubing sample lines and a passive filter system with quartz filters behind Teflon filters. Fluxes measured downwind of the manure-handling areas and water retention ponds were low compared to the barns. The reported NH_3 fluxes for milking cows, dry cows, and heifers ranged from 19 to 143 $\text{g cow}^{-1} \text{ day}^{-1}$ and emissions increased with temperature and decreased with increasing relative humidity. Annual emissions per cow would be 6.9 to 52 $\text{kg cow}^{-1} \text{ yr}^{-1}$. The dairy consisted of milking cows, dry cows, and calves and a breakdown by cow type was not reported. The filter and bubbler measurements were also compared to the NH_3 emission potential based upon N excretions (Cassel et al., 2005a). The NH_3 emission potential for the heifers, dry cows and milking cows at one dairy was 112 $\text{g NH}_3\text{-N cow}^{-1} \text{ day}^{-1}$ and for the milking cows the emissions potential was 198 $\text{g NH}_3\text{-N cow}^{-1} \text{ day}^{-1}$. Emissions were measured to be 50 $\text{g NH}_3\text{-N cow}^{-1} \text{ day}^{-1}$. For the other dairy measured the NH_3 emissions potential was 146 $\text{g NH}_3\text{-N cow}^{-1} \text{ day}^{-1}$ and for the milking cows the emissions potential was 230 $\text{g NH}_3\text{-N cow}^{-1} \text{ day}^{-1}$. Measured emissions were 103

g NH₃-N cow⁻¹ day⁻¹.

Passive diffusion samplers were used to measure average NH₃ emissions from a concrete dairy cow feeding yard in the UK. The emissions were reported to be 230 μg m⁻² s⁻¹ or 20 g NH₃ m⁻² day⁻¹ with large diurnal variations (Misselbrook et al., 2001). Wind tunnels were used to measure emissions from urine and manure spread on concrete floors. The average emission rate from the urine and manure was 49% of the applied urea-N. Cleaning was also shown to be effective at reducing emissions (Misselbrook et al., 1998).

A scale model was built to simulate a dairy-cow house and to study factors influencing emissions. Measurements showed that NH₃ emissions were greatest within two hours of applying urine to the manure on the simulated floor and declined for about 24 hours (Elzing and Monteny, 1997). A dairy stall slatted floor model was developed using a Michaelis-Menten equation to model the reaction of urea and urease. The urease activity level required for the model to reasonably predict the emissions was about 10 times higher than laboratory values most likely to build up of urea and urease on the floor (Elzing and Monteny, 1997).

A slatted floor dairy house emissions model was developed for floor and slurry pit emissions. The model was compared to monthly measurements and the error was less than ±7% (Monteny et al., 1998). The model was not sensitive to urease activity levels but was sensitive to pH. It was reported that the reliability of the model to predict emissions is dependent upon the accuracy of the model input parameters (Monteny et al., 1998). Slatted floor dairies are not common in the U.S. (USDA, 2002).

A study of the effects of dietary input and NH₃ emissions was conducted where cows were housed in small chambers and measurements were made for 48 hours. Reducing the crude protein in the diet reduced N excretions and a smaller percentage of excretions were in the urine. Despite lower N excretions the NH₃ emissions were not significantly reduced (Misselbrook et al., 2005).

A study of the effects of dietary N influences on NH₃ volatilization for Holstein heifers showed that the relationship between N intake and NH₃ volatilization was linear and most

of the UUN in the urine will be lost as NH_3 in first 24 hours (James et al., 1999). A study of the relationship between urinary N and milk urea N showed that milk urea N is not a good predictor of urinary N for estimating potential NH_3 emissions (Burgos et al., 2005).

Ammonia emissions from dairy housing areas are not well understood due to the limited number of measurements made and the large variability in dairy farming practices. Daily emission factors have been reported for open-lot dairies typical in some areas of the U.S. , but no temperature dependence was reported. Modeling NH_3 emissions from dairy housing has only been done for slatted floor dairies. Slatted floor dairies are not common in the U.S. (USDA, 2004). The slatted floor model of Monteny et al., 1998 was very sensitive to input parameters so using that model without any data on U.S. input parameters has the potential to introduce large errors in the emissions estimates.

2.7 Lagoon Emissions

Animal waste storage is another source of atmospheric NH_3 emissions due to the volatility of NH_3 in solution. Earthen lagoons or holding tanks are commonly used for long term storage of waste because of low cost and the low sludge production (Sund et al., 2001). The high nutrient concentration in waste lagoons typically means that the oxygen demand is higher than the oxygen transfer rate so lagoons are typically anaerobic (Sund et al., 2001).

Ammonia-N in waste lagoons comes from the hydrolysis of urea in urine, some of which will volatilize before it reaches the lagoon and from fecal N which is about 50% NH_4^+ and 50% protein (McCrary and Hobbs, 2001). Under anaerobic conditions ammonification also occurs where bacteria will convert the organic N to ammonia-N. Ammonification is complicated by the fact that ammonia-N is also consumed but very little research has been done looking into the ammonification rate (Grady et al., 1999). Most studies of anaerobic lagoons have looked at the rate of methane production for energy usage and not the rate of ammonification. The rate of bacterial gas production in anaerobic lagoons was shown to be very low and constant at temperatures below 15° C and then increased with increasing temperature (Oswald, 1968).

Anaerobic lagoons operate best at temperatures above 15° C; at lower temperatures the anaerobic bacteria are not able to metabolize the waste so there is no breakdown of the organic material (Middlebrooks et al., 1992; Gray, 2004). The relationship between liquid NH₃ and NH₄⁺ is pH dependent. At pH levels below 9.3, NH₄⁺ is dominant and at pH levels above 9.3 NH₃ is dominant (Snoeyink and Jenkins, 1980).

Anaerobic swine lagoon emissions have been studied more extensively than dairy lagoons due to concerns about odors. The EPA National Emission Inventory (NEI) uses swine emission factors for dairy emissions and scales the emissions based upon N content of the waste (EPA, 2004). Swine lagoon emissions were reported to be lagoon temperature dependent with the highest fluxes being in the summer at 81 μg m⁻² s⁻¹ and lowest in the winter 6 μg m⁻² s⁻¹ (Aneja et al., 2000). An empirical flux equation was developed

$$\log_{10}(NH_3 - Nflux) = 0.048T_l + 2.1 \quad (2.6)$$

where T_l is the lagoon temperature. It was estimated that lagoon operations accounted for approximately 33% of total NH₃ swine operation emissions for North Carolina (Aneja et al., 2000). Measured swine slurry emissions ranged from 6 to 52 μg m⁻² s⁻¹ with the highest emissions correlating to the warmest air temperatures (Dore et al., 2004).

A gradient flux method was used to measure fluxes from swine lagoons. NH₃ emissions averaged 14 μg m⁻² s⁻¹ and concentrations were correlated with wind speed and temperature. It was also reported that denitrification losses of N₂-N were as much as NH₃-N losses (Harper et al., 2000). A process model was developed, using effluent concentration, lagoon temperature, pH, and wind speed to describe emissions from a swine lagoon. The model explained 70% of the daily emissions and only 50% of the 4-hour average emissions. A statistical model with inputs of wind speed, lagoon temperature NH₄⁺ concentration and pH had a better R² than the process model but under low emissions conditions the model calculated negative emissions (DeVisscher et al., 2002).

Swine lagoon NH₃ emissions measured from primary, secondary and tertiary swine la-

goons with a dynamic chamber were correlated with lagoon temperature and ammonia-N concentration. Emissions ranged from 0.8 to 2 $\mu\text{g m}^{-2} \text{s}^{-1}$. The pH ranged from 6.8 to 8.1 but was not used in the empirical emissions model (Aneja et al., 2001a). A model of NH_3 emissions from swine lagoons showed an exponential increase in NH_3 flux with lagoon temperature and pH and a linear relationship between emissions and total ammoniacal nitrogen. It was reported that a limitation of the model is that there was zero flux at zero wind speed (Aneja et al., 2001b).

An NH_3 emission rate of 62 $\mu\text{g m}^{-2} \text{s}^{-1}$ was measured from Danish dairy slurry lagoons (Sommer et al., 1993). The Danish emission rate was used to estimate total UK emissions from dairies (Misselbrook et al., 2000). A natural crust forming over dairy slurry stores was found to reduce NH_3 emissions by 50%. The dry matter content of the slurry was the most important factor in crust formation (Misselbrook et al., 2005). A passive flux sampler was used to measure the flux from a tank with digested animal slurry and found that there were no emissions at subzero temperatures or slurry covered with straw. The summer NH_3 flux was reported to be 420 $\mu\text{g m}^{-2} \text{s}^{-1}$ (Sommer, 1997).

There is very little emissions data from dairy waste lagoons and no modeling of emissions from dairy waste lagoons. Swine lagoons have been studied but there is no analysis of how applicable it is to use swine lagoon emissions for dairy lagoon emissions. While the N concentration might be comparable, the diets are different and how that affects emissions is not known. There is a need for measurements of concentrations of ammonia-N concentrations and pH values in dairy lagoons. There is also a need for a mechanistic model of emissions that can be use for different ammonia-N concentrations and pH.

2.7.1 Lagoon Aeration

The storage and land application of animal waste is one of the largest emission sources from dairies of both NH_3 and odors (Bussink and Oenema, 1998). Many dairies in the U.S. store the manure as either a thick slurry or dilute with water and store in a lagoon. A survey

by the U.S. Department of Agriculture showed over 90% of dairies with 200 or more cows used some type of liquid manure storage system. In the western U.S., 64.5% of dairies use open pit storage lagoons (USDA, 1996). One cost effective method of lagoon management is anaerobic treatment. Anaerobic treatment requires very little maintenance, no treatment costs, sludge is minimized and nitrogen losses are minimized resulting in the need for less commercial fertilizer for crops. Most lagoons are anaerobic anyway due to the very high concentrations of nutrients. Aerobic treatment of lagoon waste eliminates NH_3 emissions because the aerobic bacteria metabolize the organic N to nitrate and nitrite instead of NH_3 and NH_4^+ , but is typically expensive (electricity).

Most of the research into agricultural wastewater lagoons have been conducted on swine lagoons and only a few studies on dairy lagoons. In one of the few studies of dairy lagoons, Sweeten and Wolf, (1994) studied dairy wastewater from three dairies with ammonium concentrations ranging from 116.5 to 356 mg L^{-1} and concentrations of NO_3^- 0.3 to 4.7 mg L^{-1} indicating they were aerobic lagoons.

Biological removal of nitrogen from wastewater is an inexpensive way of reducing the emission of NH_3 and other offensive compounds. In biological aerobic treatment the proteins and amino acids are broken down to NH_4^+ by heterotrophic bacteria and then autotrophic bacteria will further degrade the NH_4^+ into nitrite (NO_2^-) and NO_3^- . This process of nitrification depends upon the the amount of oxygen present and the time required for the degradation to take place. Nitrate is a highly mobile groundwater pollutant causing methaemoglobinaemia in small children. Nitrate removal is possible under anoxic conditions (no dissolved oxygen) where some bacteria are able to utilize as their terminal electron acceptor NO_3^- . The end products of this denitrification are N_2 , carbon dioxide, water and new bacteria cells.

Aerobic wastewater treatment is more expensive in terms of power required to deliver enough oxygen to the lagoon for aerobic conditions; it also requires more management to keep the system running properly. Aerobic treatment of piggery waste has been conducted and shown to be fast and effective at reducing odors and nitrogen, after four days of aeration

56% of the total nitrogen was converted to N_2 gas while during shorter time trials almost all nitrogen was conserved (Sneath et al., 1992).

Westerman and Zhang, (1997) attempted to determine the minimum level of oxygen required to treat dairy wastes for NH_3 and odor reduction. It has been suggested that at least 1 to 2 mg L^{-1} of oxygen of slurry be maintained in the lagoon to ensure enough oxygen for consistent treatment (NZAEI, 1984).

There is increasing interest in reducing NH_3 emissions, and aeration of waste lagoons is one method to accomplish this. While aerobic treatment of human waste is common, it is also expensive and the process must be monitored. There is increasing interest in regulating NH_3 emissions but mitigation strategies have not been tested. The actual reduction of NH_3 emissions will require effective mitigation strategies.

2.8 Slurry Application

Field waste application is another major source of NH_3 emissions from dairies. When the waste is applied to the field, the liquid NH_3 can volatilize during application or when exposed to the atmosphere on the field. Waste can be applied to fields in many different ways; it can be injected into the soil or it can be applied to the surface using various types of sprinklers or tanker trucks. The factors that influence waste emissions are application method, slurry NH_3 concentration, slurry physical and chemical composition, soil physical and chemical attributes, crop uptake rates, pasture canopy height and meteorology.

Sharpe and Harper (1997) used NH_3 concentrations at different heights and a momentum balance to calculate emissions from sprinkler application of swine effluent to oats starting to head out. During the application 13% of the NH_3 -N volatilized, an additional 69% volatilized from the ground during the first 24 hours. Broadcast spreading and band spreading were compared during summer and winter with emissions of NH_3 50% of the applied NH_4^+ during the summer and only 10% during the winter (Ferm et al., 1999). Band spreading was reported to not significantly lower emissions compared to broadcast spreading (Ferm et al.,

1999). Trail hose application was shown to reduce emissions versus splash plates (Sommer et al., 1997).

Injecting dairy waste into the soil reduced total NH_3 emissions to about 10% of applied NH_4^+ -N concentrations compared to a splash plate of about 30% for both arable land and grassland (Wulf et al., 2002a). Malgeryd (1998) also found that incorporating the slurry into the soil reduces emissions significantly due to dilution of NH_4^+ in the soil and pH buffering. Wulf et al., 2002b found that injection reduced NH_3 emissions but nitrous oxide emissions were greatly increased versus other application methods.

The lower dry matter content of swine slurry has been shown to have a lower NH_3 volatilization rate than cattle slurry (Pain et al., 1990). The emissions of NH_3 were shown to be linearly related to dry matter content for the first 6 hours after application and to be nonlinear after that (Sommer and Olesen 1991). A taller canopy height also reduced emissions and crop growth stage played a role in wheat leaf absorption of NH_3 and thus emissions (Sommer et al., 1997).

Using a spectroscopic technique to measure NH_3 and a tracer ratio emission method, swine slurry emissions of 3.0 and 1.7 $\mu\text{g m}^{-2} \text{s}^{-1}$ for day 2 and 3 after application have been reported by Galle et al., 2000. Thompson and Meisinger, 2004 measured emission rates from dairy waste application and found that the emission rate during the first 6 hours after application was 56 $\mu\text{g m}^{-2} \text{s}^{-1}$ and 6.1 $\mu\text{g m}^{-2} \text{s}^{-1}$ after that. The higher emission rates were measured during warmer temperatures: 92 $\mu\text{g m}^{-2} \text{s}^{-1}$ during the first 6 hours and 13 $\mu\text{g m}^{-2}$ after that. Yang et al., 2003 measured the flux of NH_3 from cattle slurry applied at a rate of 109 kg N ha⁻¹ with a NH_4^+ -N concentration of 1830 mg L⁻¹ (assuming a slurry density of 1 kg L⁻¹) and reported a flux for the first, second and third day of 110, 40 and 20 $\mu\text{g N m}^{-2} \text{s}^{-1}$ respectively. Injecting dairy slurry co-fermented with household waste had an emission rate of about 14 $\mu\text{g NH}_3\text{-N m}^{-2} \text{s}^{-1}$ while using a splash plate produced emissions of 97 $\mu\text{g m}^{-2} \text{s}^{-1}$ (Wulf et al., 2002a).

A livestock farm model showed that slurry emissions were influenced by amount of to-

tal ammonia-N on the surface, partitioning between NH_3 and NH_4^+ , surface resistance, soil infiltration rate, evaporation rate and precipitation (Hutchings et al., 1996). Several European slurry experiments were analyzed and modeled with a Michaelis-Menton type model and showed good agreement with measured emissions (Søgaard et al., 2002). An empirical model for emissions from trail hose application beneath a crop canopy was developed; the model explained less than 50% of the emissions during the first 24 hours after application and only 27% of the emissions during seven days of testing of swine and cattle slurry (Sommer and Olesen, 2000). Using a mechanistic model of slurry applied to bare soil showed that soil pH had a large influence on emissions; compared to measurements the model under-predicted emissions during the first day and over estimated thereafter (Génermonet and Cellier, 1997). Wu et al. (2003) developed a model for swine slurry application and found that the model was most sensitive to temperature, soil type, and slurry pH; the model performed well on half of the experimental data analyzed and over-predicted the other half. The infiltration of NH_4^+ was found to be spatially variable and unrelated to slurry, soil or climatic variable (Sommer et al., 2004). The NH_4^+ can bind to the soil which is related to the amount of clay in the soil and is temperature dependent (Nommik and Vahtras, 1982).

More research is needed into waste application emissions due to the many different types of waste application and the many different farming practices that influence emissions. Waste application emissions are dependent on the application method, ammonia-N slurry concentration differences, and differences in the field conditions. The field application emissions are the most complicated because they depend upon the infiltration rate of the NH_3 into the soil along with the interaction of NH_4^+ with the soil and the temperature of the soil. If the waste is applied to a crop, then the canopy affects the soil temperature, soil surface air flow, and uptake and emission rate differences between the soil and plants. More research is needed on the many different types of waste application and different soil types and crops as well as temperatures. For accurate air quality modeling it is also important to know the times of year when application is occurring.

2.9 Ammonia Emissions Modeling and Estimates

Global emissions of NH_3 have been estimated in order to understand the impact of NH_3 on the global production of sulphate aerosols and how that relates to the radiative balance of the planet (Bouwman et al., 1997). The EPA publishes a NH_3 National Emissions Inventory (NEI) based upon literature emission estimates, but those emissions are on an annual basis and do not account for farming practices and are not recommended for individual farm emissions estimates (EPA, 2004). The passage of the EPA $\text{PM}_{2.5}$ standard in 1997 has led to a need to know emissions on a local level so that models can predict the impacts of local emission sources on the concentrations of $\text{PM}_{2.5}$. The EPA $\text{PM}_{2.5}$ standard has daily and annual concentration limits, so emissions algorithms need to be at a minimum on a daily basis. Ammonia emissions are temperature dependent so emission algorithms need to account for the temperature effects.

Bouwman et al., 1997 estimated total N excretions for dairy cattle in North America at 80 kg N yr^{-1} based upon a live weight of 500 kg and a milk production of 15 L day^{-1} . The total NH_3 emissions were estimated to be 25 kg NH_3 yr^{-1} for dairy cows in North American and developed countries, with 62% of the emissions coming from dairy cows in stables and 38% coming from cows in the meadows. The cow assumptions used by Bouwman et al., (1997) are not accurate for the WSU dairy where the average cow weighs 720 kg and produces about 40 L of milk day^{-1} and does not spend any time in a meadow while being milked. Nennich et al., 2005 reported that N excretion was a function of feed intake, protein intake, and body weight. Using the equation developed by Nennich et al., 2005 and the WSU dairy cow data, the daily N excretion is 560 g cow^{-1} day^{-1} with annual N excretions of 200 kg yr^{-1} . Based upon the data from one dairy, the N excretion number used by Bouwman et al., (1997) of 80 kg is low by at least a factor of 2. If emissions are calculated as a percentage of N excreted then emissions will be understated by at least a factor of 2.

The dairy NH_3 annual emissions estimated in the NEI are based upon different farming practices from European research (EPA, 2004). The NEI NH_3 estimate for dairy cows is 38

kg yr⁻¹. The NEI estimate of emissions was performed by first estimating N excretion per animal mass and then estimating a percentage of the N mass emitted from different housing, storage and waste application types. The NEI emissions in some cases use swine emission percentages for different farming practices where data is not available for dairies. The use of standard N excretion estimates is not accurate for high production dairy cows and using body weight as the only factor is not an accurate indicator of excretions (Nennich et al., 2005). The NEI does not account for seasonal differences in emissions.

An inverse modeling approach was used to determine the seasonality of emissions in the eastern U.S. by using wet deposition NH₄⁺ data and the Community Multiscale Air Quality (CMAQ) model to back calculate NH₃ emissions (Guilliland et al., 2003). The model showed emissions were lower by 75% during the winter compared to summer and that the NEI for 1990 was high by 20% for cattle and swine. A study of NH₃ deposition showed that there is a high degree of variability in local deposition (Sutton et al., 1998). Modeling of the deposition on a 20 km grid did not show much variability but, on a 5 km grid there was large variability. Measurements showed a large concentration gradient within 500 m of the NH₃ emission source. It was also reported that deposition was land-cover dependent and that using simple deposition methods such as fixed deposition velocities might lead to erroneous results.

A dairy farm process NH₃ emissions model was developed for the U.S. based upon European emissions (Pinder et al., 2004a). The model only considers NH₃ emissions from urinary urea and not the the microbiological conversion of organic N to NH₃. The model uses a milk production of 27.2 kg milk cow⁻¹ day⁻¹ and a daily excretion of N to be 256 g N cow⁻¹ day⁻¹. The process model reported annual dairy cow emissions of between 18 and 36 kg NH₃ cow⁻¹ yr⁻¹ (Pinder et al., 2004b). Emissions were highest in warmer climates and were also highest in the summer during waste application.

High time resolution and meteorological dependent modeling of NH₃ emissions is important for accurate PM_{2.5} modeling. Most current emission models report results on a annual

basis, not taking into account meteorology and most models do not account for differences in cow diet, weight and milk production that influence N excretion amounts. There is a need for a high time resolution NH_3 emissions model that takes into account farming and cow factors that influence emissions.

Chapter 3

Methodology

The WSU Dairy Ammonia Emissions Project employed a state of the art spectroscopic technique to measure NH_3 concentrations. Ammonia concentrations were used with an area source tracer ratio method to calculate fluxes. Data were collected at the WSU Knott Dairy Center located 8 km south of Pullman, Washington.

3.1 Differential Optical Absorption Spectroscopy

The measurement of atmospheric gases is challenging due to the low concentrations of many gases of interest and the number of species in the atmosphere. Measurement techniques must therefore be sensitive at the ppbv or pptv level and be must be specific to the species of interest. No one measurement technique will measure all species at the required concentration levels. Ammonia is particularly difficult to measure due to its adherence to surfaces which creates measurement artifacts for instruments with inlets; it will stick to inlet walls and come off depending upon the concentration on the wall and in the air stream. Since the inlet artifacts make most measurements of NH_3 unreliable, an in-situ measurement method without inlets would improve the reliability of NH_3 measurements. Open-path spectroscopy is one measurement method that is ideal for the measurement of NH_3 .

Spectroscopy is the study of the interaction of matter with electromagnetic radiation and it provides one method to measure atmospheric gases. Gas molecules can absorb radiation if the radiation can electronically excite or change the vibrational or rotational energy of the molecule. By measuring the spectrum of radiation before and after the trace gas absorption, it is possible to calculate a concentration using Beer's Law. Differential optical absorption spectroscopy (DOAS) measures the spectroscopic molecular absorption of trace gases over an open atmospheric path. DOAS can be used for molecules that show differential photoab-

sorption over the spectral bandpass of spectrograph. An absorber that attenuates radiation, but has no molecular spectral structure over the measurement wavelength is not suitable for measurement by DOAS. The differential structure of the absorption, not the absolute attenuation of the radiation over the measured path, eliminates the need for knowing the instrument transmission properties. Continuum attenuation only decreases the signal level.

Thus, one benefit of DOAS is that it does not require total understanding of the calibration of the instrument or the transmission properties of the instrument. The instrument must maintain relative spectral stability over the measurement period, but that is all that is required. The advantages of DOAS include: (1) in-situ measurement, (2) selectivity (many wavelengths measured at once), (3) simultaneous multiple species measurement possible, and (4) self-calibrating measurement which only depends upon the absolute cross section of the gas being measured. The disadvantages include, (1) measurement over a light path that spatially averages and not at a point, (2) not all species can be measured, and (3) not as sensitive as some other methods.

The absorption of radiation through a medium, in this case air, can be expressed by the Beer-Lambert absorption law. The Beer-Lambert law for a spectrum of wavelengths is used to calculate the concentration of the gas of interest as explained below:

$$I(\lambda) = I_o(\lambda)exp[-L \times \sigma(\lambda) \times c] \quad (3.1)$$

- λ - wavelength;
- $I(\lambda)$ - radiation intensity in the presence of absorbers;
- $I_o(\lambda)$ - radiation intensity without absorbers;
- L - optical path length;
- $\sigma(\lambda)$ - absorption cross section of absorber;
- c - concentration of absorber.

In the atmosphere there are many species that absorb radiation so the equation above must be modified to include all absorbing species.

$$I(\lambda) = I_o(\lambda)exp[-L \times \Sigma_i \sigma_i(\lambda) \times c_i] \quad (3.2)$$

where the subscript i denotes each species that absorbs over the wavelength region of interest. Thus, it is important to know the other species that might absorb over the wavelength region measured and account for them in the analysis if they have similar absorption structures.

In addition to other atmospheric species, there are also other processes in the atmosphere that influence the spectrum measured by the instrument. Rayleigh scattering in the atmosphere is the scattering of light as it passes through the atmosphere by small molecules and acts as a continuum absorption as seen by the instrument. Rayleigh scattering can be modeled as a cross section according to the following equation:

$$\sigma_R(\lambda) \approx \sigma_{RO} \times \lambda^{-4} \quad (\sigma_{RO} \approx 4.4 \times 10^{-16} \text{ cm}^2 \text{ nm}^4 \text{ for air}) \quad (3.3)$$

Penndorf in 1957 derived a more accurate equation coming up with the Rayleigh extinction coefficient $\varepsilon_R(\lambda)$ which is related to the concentration of air molecules in the atmosphere.

$$\varepsilon_R(\lambda) = \sigma_R(\lambda) \times c_{air} \quad (3.4)$$

Where c_{air} is $2.4 \times 10^{19} \text{ cm}^{-3}$ at 20°C and 1 atmosphere.

In addition to absorption by Rayleigh scattering there is also wavelength dependent continuum scattering by aerosol particles called Mie scattering. Using the same reasoning as with Rayleigh scattering, Mie scattering can be treated as an absorption process. Mie scattering can be simulated as a linear absorption across the measurement spectrum. Thus, the Beer-Lambert law becomes the following with the addition of other absorbers denoted by the subscript i .

$$\ln \left(\frac{I(\lambda)}{I_o(\lambda)} \right) = exp[(-L \times \Sigma(\sigma_i(\lambda) \times c_i) + \varepsilon_R(\lambda) + \varepsilon_M(\lambda))] \quad (3.5)$$

Since there are many variables and uncertainties and errors in the above equation it is not possible to exactly solve the Beer-Lambert law. For example $I(\lambda)$ and $I_o(\lambda)$ are generally not measured over the same path so there may be illumination differences inside the instrument which affect the spectral residual analysis. It is possible that there are unknown absorbers and instrument changes due to temperature that occur between measurement of I and I_o . Instrument spectral stability is important to calculating correct concentrations.

3.1.1 Instrumentation

The WSU dairy NH_3 emission project employed a state of the art measurement system constructed at WSU for the measurement of NH_3 . The instrument and setup are described in detail by Mount et al. (2002). A brief description follows.

The first component of the NH_3 DOAS system is a continuum light source with very low spectral modulation in the region of interest. A 150 W Xe high pressure arc lamp (Hamamatsu, model L273) was tested against a deuterium lamp and found to be more stable with a higher UV output. In addition it is a very small source (0.5 mm) so that when it is imaged on the spectrograph entrance slit light throughput is maximized.

A picture of the instrument is shown in Figure 3.1. The light from the Xe lamp is directed onto a $f/5$ parabolic mirror 40 cm diameter built by Colorado Precision Optics of Longmont Colorado. To simplify the optical design the primary mirror was used both as the transmitting mirror and the receiving mirror for the spectrograph which reduces the cost and makes alignment much simpler. The lamp was positioned at the side of the optical path of the primary mirror and a folding mirror was used to direct the light beam onto the primary mirror optical axis. The lamp only illuminates an annulus of about 6 cm on the outer edge of the mirror due to another folding mirror used to image the light onto the spectrograph entrance slit blocking most of the light from the lamp. The outer annulus of light is directed out over the measurement path to four 12.7 cm retroreflectors (Melles-Griot, Inc., Carlsbad, California) positioned on a tripod. Retroreflectors were chosen instead of a steerable mirror

system because alignment is greatly simplified. The retroreflectors are coated with Al with a protective overcoating of Mg. The light from the retroreflectors illuminates the inner annulus of the primary mirror by translating the light from the outer annulus. The light is then intercepted by the folding flat and directed into the spectrograph. A Zn emission lamp is placed at the folding flat in front of the spectrograph and provides a spectral fiducial at 213.9 nm.

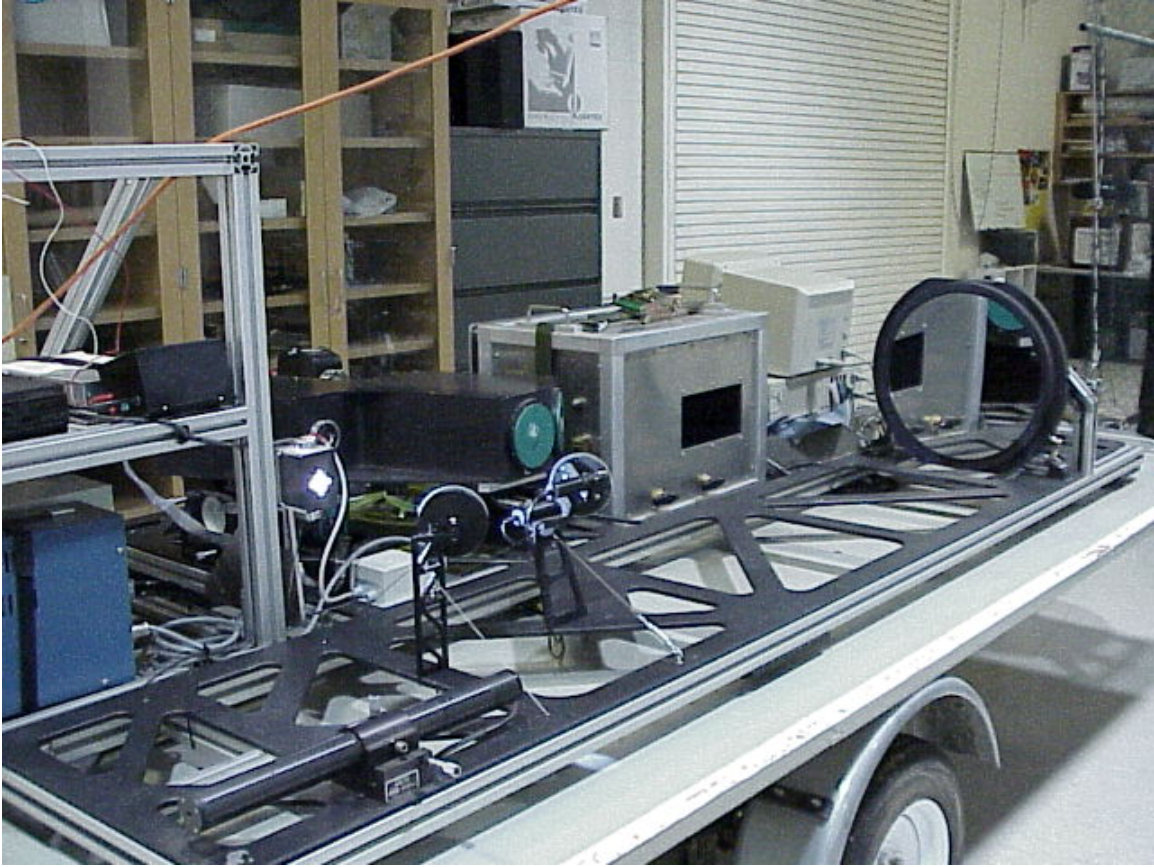


Figure 3.1: WSU NH_3 instrument. The Xe light source at the left illuminating the folding mirror used to direct the beam to the telescope on the right. The mirror used to direct the light to the spectrograph is to the right of the folding mirror. The spectrograph is the black instrument above and to the right of the light source and the entrance slit is above the light source.

The spectrograph is a homebuilt double crossed Czerny-Turner with a focal length of 37.5 cm on each side. The spectrograph was designed to minimize scattered light (always a problem in the UV) and aberrations in the focal plane. The spectrograph has a sampling

of 8 detector pixels at full-width at half-maximum of a spectral line. The spectral coverage is about 42 nm. The spectral resolution is 1 nm. The detector is a homebuilt Reticon silicon photodiode array with 1024 pixels with each pixel 25 μm wide and 2.5 mm high. The detector has a 16-bit analog-to-digital converter, and is digitized at 1000 detected electrons to produce a data number (DN). The leakage noise of the detector is 0.004 DN s^{-1} pixel $^{-1}$. The readout noise is 3 DN out of 2^{16} . The largest variation in instrument precision is caused by illumination changes on the optics caused by thermals in the atmosphere and which results in a spectral residual of 0.1%.

3.1.2 Data Collection

The absolute NH_3 cross section (cm^2) was measured in the laboratory in 1999 prior to the start of measurements at the WSU dairy. Five strong absorption features were measured from 200 to 220 nm with the strongest features at the shorter wavelengths. The advantage of measuring the cross section with the field instrument is that the instrument spectral aberration function is then built into the measured cross section so no error in convolving the instrument function and the cross section is introduced. The NH_3 cross section was measured in a 27 cm quartz cell with a calibrated bottle of NH_3 in N_2 from Scott Specialty Gas, Inc. with a $\pm 5\%$ calibration. Ammonia was continuously flowed through the cell to ensure the wall losses would be stabilized. The differential cross section compared to within $\pm 20\%$ (Mount et al., 2002) with the published cross sections of (Mellqvist and Rosen, 1996; Suto and Lee, 1983). In addition to NH_3 , SO_2 , and NO cross sections were also measured since they have absorption spectral features in the same wavelength region as NH_3 . Due to the fact that we are measuring NH_3 absorption in the mid-ultraviolet below the atmospheric cutoff there is no solar spectrum structure seen in the spectrum, a major analysis advantage.

A background I_o (see Equation 3.5) was taken at the WSU campus with a measurement path of 16 m and also upwind of the dairy using approximately a 100 m path both ways. The backgrounds showed no absorption features of NH_3 to a level of 2 ppbv. The WSU

dairy background was used for most of the data analysis since it had a similar path length to most measurements and better simulates the illumination of the spectrograph while making measurements.

Prior to the collection of data the instrument dark current is always measured. The dark current is electronic noise in the system. A dark spectra is taken by putting a black slide in front of the entrance slit of the spectrometer before the actual measurement spectra is taken and this is subtracted from the measured spectrum. The time resolution of the dark current was approximately 1 second. One hundred dark spectra are co-added and averaged to get the dark spectra. The dark current is removed by the data analysis software. The dark current measurement also removes diode to diode variations in the readout of the detector (Harder et al., 1997).

Data collection consisted of aligning the instrument pointing to the retro mirrors so that the counts were maximized. The spectra averaging time was adjusted so that the maximum count rate was about 40000. The averaging time ranged from less than 0.5 second to a few seconds depending upon the path length and how well the instrument could be aligned over the light path. The number of spectra coadded was then determine so that the data was averaged over five minute time intervals. The grating was also adjusted so that Zn fiducial line peaked and remained at pixel 613. The count rate and the Zn line were checked periodically to ensure that the count rate was near 40000 and the center of the Zn line was at pixel 613. Temperature changes and settling of the trailer tended to shift the alignment of the beam off of the retros and thus off the entrance slit. Temperature also affected the spectrograph and shifted the Zn line from pixel 613; the largest shifts occurred when the temperature was changing the fastest during the day. Notes were made in the data record when the grating or trailer were adjusted so that those records were not used as a relative I_0 as explained below.

3.1.3 Data Analysis

To calculate concentrations using DOAS the Beer-Lambert law is used to convert absorbance to concentrations. A least squares fitting routine is used to solve the Beer-Lambert law, the program used for this project was developed by Dr. Arthur Schmeltkopf and is described in detail by Harder et al. (1997).

Data analysis was performed in two steps to improve the accuracy of the measurements. Harder et al. (1997) reported that performing the data analysis in two steps resulted in lower overall residuals. The first step is to use a relative I_o taken during the day of measurements, that is an I_o from the measurement data with NH_3 features present in the spectra. This relative I_o is used for initial data reducing and the concentration of NH_3 is calculated relative to the I_o chosen. Then the relative I_o is analyzed using an absolute I_o with no NH_3 and the true concentration of the relative I_o is calculated. As Harder et al., 1997 noted this has the advantage that illumination is the same for the initial reduction. This method was also advantageous because the cross section did not have the Zn lamp line in it so reducing the NH_3 data against itself with the Zn fiducial line in it help align the spectra. A relative I_o was chosen by looking for periods when the counts were high and not immediately before or after adjusting the instrument. During the slurry experiment when concentrations ranged from over 1 ppmv to less than 20 ppbv, multiple relative I_o s were chosen. Analysis of the choice of relative I_o 's showed that concentrations were within $\pm 15\%$.

The wavelength region used in the analysis depended upon the NH_3 concentrations reflected as spectral line depth. Data analysis showed that at high concentrations of NH_3 some of the stronger NH_3 absorption lines did not increase linearly with concentration. The high concentrations observed in the stalls were analyzed using the spectra from 211 to 220 nm and contained two NH_3 absorption features. The lagoon data was analyzed using the region 207 to 220 nm and it contained three absorption features.

Once a relative I_o was chosen the software allows for various physical changes to the spectra to be removed to improve the fitting. All spectra were smoothed with an 8 point

Gaussian curve to take out noise in the spectra. The absorption features of NH_3 are very broad (predissociated) so very little spectral information is lost in the smoothing process. Another complication is that the spectra can be shifted due to small angular displacements of the grating drive and thermal stresses on the spectrograph (Harder et al., 1997). The spectra can also be stretched by instrument variations mainly caused by temperature (Harder et al., 1997). Spectra shifting and stretching was enabled to improve the fitting and reduce the spectral residuals.

The solution is achieved iteratively by the modified Nash-Marquardt method (Nash, 1990). A minimum of the sum of the squares of the residual is used to determine the solution. The residual was monitored during the fitting to look for line saturation, other molecular absorbers, or trends to indicate a problem. Residual analysis identified the saturation of the NH_3 line at 208 nm in the stalls. No other molecular absorption features were observed so no other molecules were added to the fitting routine.

The short-path DOAS technique proved to be a very effective method to measure NH_3 from the WSU dairy. It was sensitive enough to measure down to a few ppbv and up to a few ppmv. The instrument was very reliable. The DOAS concentration NH_3 concentration data were combined with an area source tracer ratio method to calculate emission fluxes from the housing, waste lagoons, and waste application.

3.2 Area Source Tracer Techniques

Measuring the emission rates of NH_3 into the atmosphere is very important to understand the impacts on atmospheric chemistry and the environment. The measurement of atmospheric emissions is not easy due to the turbulence of the atmosphere. The short-path DOAS concentration measurement of NH_3 requires a flux measurement technique that does not rely on point source measurements. An area source tracer method was selected to measure the fluxes from the housing stalls, waste lagoons, and grass fields after waste application.

Atmospheric tracers are used to determine the transport and dilution processes of the

atmosphere. Ludwig et al. (1983) developed a tracer ratio method for the measurement of fluxes from area sources and point sources that were inaccessible. The tracer ratio method involves releasing a tracer gas at a known release rate upwind of the emission source and then measuring the tracer and the gas of interest simultaneously downwind. The tracer data is used to determine the turbulent diffusion of the atmosphere. Sulfur hexafluoride (SF_6) was chosen as the tracer gas because it is slow to react and therefore will not affect the calculation of the NH_3 fluxes. The higher molecular weight of SF_6 compared to NH_3 has a negligible effect due to turbulent diffusion being the dominant transport mechanism (Kaharabata et al., 2000). The technique has been used successfully to measure emissions from various area sources (Lamb et al., 1995; Shorter et al., 1997; Howard et al., 1992; Eklund, 1999). The best conditions for tracer experiments are with a steady wind so there is good turbulent mixing and small σ_θ so that the tracer gas plume mixes thoroughly with the NH_3 plume.

The method builds on the Gaussian plume equation of Turner (1970) that describes the steady-state concentration downwind of an emission source. The equation for the concentration downwind of a line source is the following.

$$C_l = \frac{2Q_l}{\sin\Phi u \sigma_z \sqrt{2\pi}} \quad (3.6)$$

C_l - line source concentration at ground level (g m^{-3})

Q_l - line source emission rate ($\text{g m}^{-1} \text{s}^{-1}$)

Φ - angle between wind direction and line source direction

u - windspeed (m s^{-1})

σ_z - standard deviation of Gaussian vertical concentration distribution

An approximation of the vertical standard deviation can be made by using the following equation

$$\sigma_z(x) = ax^b \quad (3.7)$$

Table 3.1: Suggested variables for calculating σ_z based upon stability from Busse and Zimmerman, (1973).

Atmospheric Stability	a	b
Extremely unstable	0.25×10^{-3}	2.09
Moderately unstable	0.0049	1.11
Slightly unstable	0.10	0.93
Neutral (day)	0.26	0.69
Neutral (night)	0.25	0.63
Stable	0.20	0.60

where the distance downwind of the source is denoted by x and the coefficients a and b are empirical. The diffusion coefficients can be calculated or found in the literature. The coefficients found by Busse and Zimmerman, (1973) are shown in Table 3.1.

Substituting into the above equation gives a function that relates dispersion to distance from the source.

$$C_l = \frac{2Q_l}{\sin\Phi u a x^b \sqrt{2\pi}} \quad (3.8)$$

For an area source the line source equation can be integrated to get the concentration downwind of an area source.

$$C_A = \frac{2Q_A(X_u^{1-b} - X_d^{1-b})}{\sin\Phi u a (1-b)\sqrt{2\pi}} \quad \text{for } b \neq 1 \quad (3.9)$$

C_A - area source concentration at ground level (g m^{-3})

Q_A - area source emission rate ($\text{g m}^{-1} \text{s}^{-1}$)

X_u - distance to upwind edge of area source (m)

X_d - distance to downwind edge of area source (m)

The area source and line source equations can be combined to solve for the flux from the area source, the only unmeasured variable is b which depends upon stability and vertical mixing.

$$Q_A = \frac{C_A Q_l (1 - b)}{C_l (X_u^{1-b} - X_d^{1-b}) x^b} \quad (3.10)$$

One source of error is the approximation of σ_z . Experimental conditions might differ from the conditions from which a and b were derived by Busse and Zimmerman, (1973). Using the tracer data and the line source equation it is possible to calculate σ_z .

In addition to the line source method a point source method was used in the milking cow stalls. The point source method is advantageous since there is no requirement for atmospheric dispersion variables. Lecture bottles of SF₆ with a series small restrictors were used as point sources spread throughout the source area so differences in turbulence in the stalls was taken into account. The method, outlined by Kaharabata et al., (2000), was used where a series of point sources were released in the cow stalls and then measured along the instrument path. The equation for the point source flux method is

$$Q_{NH_3} = \frac{Q_{SF_6} C_{NH_3}}{C_{SF_6}} \quad (3.11)$$

where Q is the flux of the gas ($g\ s^{-1}$) and C is the concentration ($g\ m^{-3}$).

The use of an area source tracer method to measure NH₃ fluxes from the WSU dairy was very successful. Using the tracer data to determine σ_z and revise the values of a and b based upon wind speed better modeled the vertical diffusion and reduced error between modeled and measured concentrations. The point source method is particularly effective for determining fluxes but since the method does not give any information about atmospheric turbulence it is not optimal for modeling emissions.

3.3 WSU Dairy

The WSU Knott Dairy Center is a research and commercial dairy that also serves as a teaching and research laboratory in addition to supplying milk for the WSU creamery. The milk from the dairy is processed on campus and sold as cheese; students manage and take

care of their own small herd and research is conducted on diet, milk production, waste production and cow health. The WSU dairy is located 8 km south of Pullman, Washington U.S. (N 46° 43.8', W 117° 10.1'). It has approximately 175 Holstein milking cows, 35 dry cows, 130 heifers and 75 calves.

The milking cows are housed in three-sided freestall barns with concrete floors. Waste, which includes milking cow manure and urine, bedding and milking parlor wash water from the stalls, is scraped into pits daily. The pits are flushed with recycled wastewater and the wastewater goes to a solids separator where solids greater than 0.3 cm in diameter are removed. From the solids separator the wastewater goes to a high solids lagoon (250 m³) where additional solids are removed via gravity settling. The supernatant from the high solids lagoon goes to the low solids lagoon (9500 m³) where additional settling occurs. The low solids lagoon is used as the primary storage lagoon for waste from the dairy. Two additional lagoons (19000 m³) are used for long term storage of waste until the waste is applied to the surrounding grass fields in the late summer and early fall.

The milking cows are fed a diet of 26 kg of feed per day on a dry matter basis, with a diet of 19% crude protein. The feed consists of alfalfa silage (25.6%), alfalfa hay (22.3%), concentrate (35.7%), wheat mill run (6.6%), and whole cottonseeds (9.9%). The crude protein in the feed is approximately 19%. The cows consume 475 g day⁻¹ of K and 790 g day⁻¹ of N. The daily consumption of Na is estimated to be 83 g day⁻¹, but it varies as the cows have unlimited access to salt. The daily milk production for the herd averages about 41 kg cow⁻¹. Nennich et al. (2005) reported an average milk production of 31.4 kg day⁻¹ with a standard deviation of 11.0 kg day⁻¹ for 553 cows sampled for predicting nutrient excretions.

The low solids lagoon was extensively sampled in 2001 as described by Neger (2002). The average ammonia-N concentration in the lagoon was 670 mg N L⁻¹ and the average total Kjeldahl N (TKN) concentration was 1025 mg N L⁻¹. Lagoon pH averaged 7.8. No detectable amounts of dissolved oxygen, nitrate, or nitrite were measured. In addition to N

Table 3.2: Nitrogen mass balance for the milking cows and waste treatment system of the WSU Knott Dairy Center. Nitrogen imports are additions to the milking cow stall area or the waste lagoon system and exports are subtractions from the stalls or lagoon system not accounting for volatilization.

Imports	kg N yr⁻¹
Feed	51000
Bedding	1900
New Cows - Heifers	1100
Total Imports	54000
Exports	
Milk	11500
Solids	7700
Culled Cows	1100
Calves	200
Nitrogen in Lagoons	27000
Total Exports	20500
Maximum Nitrogen Stall Emissions	6500

sampling the solids blanket at the bottom of the lagoon was measured. In general most of the solids settled out within 40 m of the lagoon inlet.

3.3.1 Nitrogen Mass Balance: A Test For Measured Total Emissions

A independent method of calculating stall emissions is to compute inputs and exports of N to the stall area. Ammonia is the dominant volatile species in the stalls, so it was assumed that all N lost was in the form of NH₃. Due to difficulties in estimating some of the amounts used in the analysis (see below), the error of the mass balance is approximately ±20%. The results are shown in Table 4.1 and explained below.

The main N import is feed. There are 175 cows each being fed daily 26 kg of feed on a dry matter basis. The feed is approximately 19% crude protein. Total N is calculated by dividing the crude protein by 6.25 (NRC, 2001). This gives an annual milking cow N intake of 51000 kg. Compost is used as bedding at the WSU dairy and is disposed of with the waste, so it has the potential to enter the lagoon system. The dairy uses 666800 kg of compost per

year which is 41.2% dry matter, and of that 0.7% is N for a total of 1,900 kg of N. Sixty fresh heifers are added each year and they each weigh 600 kg with a body composition of 2.88% N for an import of 1100 kg (Kohn, 2002). Runoff from the dry cow and heifer barns drains into the waste lagoons but the annual N amount is estimated to be less than 100 kg.

Exports from the milking cow stall area and the waste system include milk, waste, calves, and culled cows. The average milk production per year for the entire dairy is 2172300 kg with a milk protein content of 3.30%. The average milk production per cow is 10300 kg per year. This gives an N export in milk of about 11500 kg per year. The N in the waste can either volatilize, be composted or go into the lagoon system. The total solids exported from the dairy is 2880000 kg which is 26.1% dry matter and the dry matter is 1.14% N. This gives a total N export of solids of 8600 kg with approximately 10% of that coming from the dry cow and heifer barns.

Calves born each year number 175, with an average weight of 41 kg. Sixty milking cows are culled each year with a weight of 635 kg each. Assuming a N body percentage of 2.53% for calves and 2.88% for culled cows the total nitrogen exports are 200 kg N and 1100 kg N exported for calves and culled cows respectively (Kohn, 2002). The total liquid volume of the lagoons is 29,000 m³. The measured average N concentration is 1025 mg L⁻¹ which gives a total waste N in the lagoons of 30000 kg N with a holdover from the previous year of 2700 kg N. Thus, the total N added during the year is approximately 27000 kg N. An unknown amount of N remains in the lagoon as solids; it could not be accurately estimated but has only a small effect on the computations. The difference between nitrogen unaccounted for and the amount in the lagoons should be the maximum N emitted from the stalls and that is 6500 kg N or 7900 kg NH₃.

For the slurry application the total volume of the lagoons and the concentrations of ammonia-N in the slurry can be used to calculate the slurry application emissions. Waste from the lagoons is applied to nearby grass fields and used as fertilizer. The WSU dairy uses a "Big Gun" sprinkler (Nelson Irrigation, Walla Walla, Washington) on a traveling reel.

The sprinkler has a coverage radius of 50 m depending upon wind conditions. The pump has a discharge of $95 \text{ m}^3 \text{ hr}^{-1}$. The sprinkler reel has 280 m of hose and the area applied during application is approximately 32000 m^2 . The dairy has four storage lagoons with a total capacity of 29000 m^3 . About 2000 m^3 of slurry is left in the lagoons at the end of application to use as recycled wash water. It takes one month to empty the lagoons and during that time about another 2000 m^3 of waste is added to the lagoons. The total volume of slurry applied to the fields is then 29000 m^3 . For the field emissions slurry is applied to 32000 m^2 daily and it takes about 30 days to complete the job.

The WSU Knott Dairy Center is a very good location to study NH_3 emissions. There are no NH_3 emission sources in the area so background concentrations were below the instrument detection limit of 2 ppbv. West winds are fairly common so interference free measurements are possible. The dairy is a research dairy so information about farming practices was easily obtained, and the staff was very willing to accommodate the measurements.

Chapter 4

Housing Emissions

Measurement and Modeling of Atmospheric Flux of Ammonia from Dairy Milking Cow
Housing

Brian Rumburg, George H. Mount, Brian Lamb, Hal Westberg, Jenny Filipy, David Yonge

Department of Civil and Environmental Engineering

Ron Kincaid, Kristen Johnson

Department of Animal Sciences
Washington State University
Pullman, Washington 99164-2910

to be submitted to
Atmospheric Environment

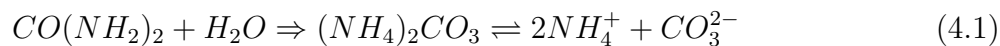
4.1 Abstract

Atmospheric ammonia (NH_3) measurements are needed to better understand the impacts of NH_3 emissions on aerosol formation and concentrations and anthropogenic changes to the N cycle. This paper describes concentration measurements of NH_3 using differential optical absorption spectroscopy (DOAS), tracer ratio flux experiments, and development of a NH_3 emissions model from a dairy milking cow free stall house with concrete floors. An area source tracer gas ratio method was used to determine NH_3 fluxes which involved releasing SF_6 as the tracer gas from the upwind edge of the stalls and measuring the tracer concentration downwind along with the DOAS NH_3 measurements. The flux is calculated from the ratio of the NH_3 and SF_6 concentrations and the SF_6 release rate and taking into account the differences in area and dispersion. The measured stall flux for the summers averaged $8.1 \pm 5.2 \text{ mg NH}_3 \text{ cow}^{-1} \text{ s}^{-1}$ at an average temperature of $18 \pm 5^\circ \text{ C}$. The emissions model calculated liquid NH_3 concentrations in urine puddles, NH_3 volatilization, mass transfer to the bulk atmosphere, and NH_3 transport. The predicted concentrations were within $\pm 30\%$ of the measured concentrations. Total annual NH_3 emissions for the dairy of 175 milking cows was 7000 kg or $40 \text{ kg NH}_3 \text{ cow}^{-1} \text{ year}^{-1}$. The maximum stall emissions based upon an independent calculation of a N mass balance was 7900 kg NH_3 per year. The model was very sensitive to urine puddle pH and also showed that emissions are temperature dependent.

4.2 Introduction

Atmospheric ammonia (NH_3) emissions affect the environment and human health in ways that are not fully understood due to a lack measurement data and time resolved emission algorithms. The lack of data in the U.S. has led to large uncertainties in estimates of emission rates, and the factors that influence emissions, which make regulating and mitigating emissions difficult (NRC, 2003). The NRC (2003) listed NH_3 as the most important atmospheric gas emitted from animal feeding operations in the U.S. due to impacts related to deposition and haze. In the atmosphere, NH_3 primarily reacts to form ammonium sulfate and ammonium nitrate aerosols which are regulated as part of the U.S. Environmental Protection Agency National Ambient Air Quality Standards $\text{PM}_{2.5}$ (particulate with an aerodynamic diameter less than 2.5 microns). Thus, NH_3 emissions are important due to their precursor status.

Global atmospheric emissions of $\text{NH}_3\text{-N}$ are estimated in the range of 45 to 54 Tg N yr^{-1} (Dentener and Crutzen, 1994; Bouwman et al., 1997; van Aardenne et al., 2001). Emissions from agriculture are the largest source, at 79% of the global total, with about 50% from animals (van Aardenne et al., 2001). The N in animal waste can form NH_3 ; one pathway is the reaction of urea in the urine with urease in the manure or soil and another is the microbiological breakdown of organic N under anaerobic conditions. The fastest reaction pathway for the formation of NH_3 is reaction of urea and urease. Urinary urea-N (UUN) will react with the enzyme urease to form ammonium (NH_4^+):



Aqueous NH_4^+ can dissociate to form NH_3 depending upon the pH of the solution and NH_3 can volatilize into the atmosphere depending upon the temperature and mass transfer to the free atmosphere.

Milking cows have the largest per animal emissions of NH_3 due to the energy and pro-

tein required for milk production. A study of the effects of dietary N influences on NH_3 volatilization for Holstein heifers showed that the relationship between N intake and NH_3 volatilization was linear and most of the UUN in the manure will be lost as NH_3 within first 24 hours (James et al., 1999). Misselbrook et al., (2005) reported that reducing the dietary crude protein reduced total N excretions and UUN, but did not reduce NH_3 emissions.

Cassel et al., (2005) measured NH_3 fluxes for a dry lot dairy with milking cows, dry cows and heifers and emissions ranged from 19 to 143 g head⁻¹ day⁻¹. Average NH_3 emissions from a concrete dairy cow feeding yard were reported to be 230 $\mu\text{g m}^{-2} \text{s}^{-1}$ with large diurnal variations (Misselbrook et al., 2001). A dairy stall slatted floor model was developed using a Michaelis-Menten equation to model the reaction of urea from the urine and urease from the manure. The urease activity level required for the model to reasonably predict the emissions was about 10 times higher than laboratory values and was most likely caused by an excess of urea and urease on the floor versus the laboratory (Elzing and Monteny, 1997). A slatted floor dairy house emissions model for floor and slurry pit emissions showed good agreement with measurements (Monteny et al., 1998). Hood experiments showed that 49% of the urea-N applied to a floor plot volatilizes and that cleaning the area reduced emissions (Misselbrook et al., 1998). A model dairy cow house was used to simulate NH_3 emissions using different fouling methods, a decay in emissions with time was reported and an empirical model was developed (Elzing and Monteny, 1997).

This work is part of a series of papers on the emissions of NH_3 from the dairy cows at the Washington State University (WSU) dairy. The purpose is to determine the total NH_3 emissions of milking dairy cows and develop an emissions model for use in a regional air quality model. The other sources being measured include the wastewater lagoons (Rumburg et al., 2006) and sprinkler application of wastewater (Rumburg et al., 2005). An area source tracer ratio technique was used to determine fluxes from the stalls and to calibrate a Gaussian plume dispersion model which was used to determine fluxes when tracer experiments were not being conducted. A cow N excretion model was developed to calculate aqueous ammonia-

N (NH_4^+ and NH_3) concentrations in the urine puddles, and chemical and meteorological parameters were used to calculate NH_3 volatilization. For this paper, the objectives were to measure the NH_3 emissions from the dairy cow stalls and develop emission algorithms for use in air quality modeling. This paper discusses the measurement emissions from the dairy cow stalls and the development of the emission model.

4.3 Experimental

Tracer ratio experiments and concentration measurements of NH_3 were made downwind of the north milking cow stalls at the WSU dairy from 2001 to 2004. Measurements could not be made downwind of both stalls at WSU due to saturation of the absorption features at high concentrations. Measurements were made for 31 days mainly during the summer with a few measurements during the winter.

4.3.1 Dairy Information

The WSU dairy is located 8 km south of Pullman, Washington U.S. (N $46^\circ 43.8'$, W $117^\circ 10.1'$). It has approximately 175 Holstein milking cows. A schematic of the dairy stall area is shown in Figure 4.1. The milking cows are housed in three-sided freestall barns with concrete floors. The north stalls where the measurements were made houses 100 cows in an area of 1100 m^2 with an additional 300 m^2 used for bedding areas. The waste and used bedding is scraped daily into waste pits. The milking cows are fed a diet of 26 kg of feed per day on a dry matter basis, the crude protein of the diet is 19%. The feed consists of alfalfa silage (25.6%), alfalfa hay (22.3%), concentrate (35.7%), wheat mill run (6.6%), and whole cottonseeds (9.9%). The cows consume 475 g day^{-1} of K and 790 g day^{-1} of N. The daily consumption of Na is estimated to be 83 g day^{-1} , but it varies since the cows have unlimited access to salt. The daily milk production for the herd averages $41 \text{ kg cow}^{-1} \text{ day}^{-1}$.

Figure 4.2 shows the experimental set up with the DOAS instrument housed in the trailer at the left and the retroreflectors to the right. The tracer gas syringe samplers are on the

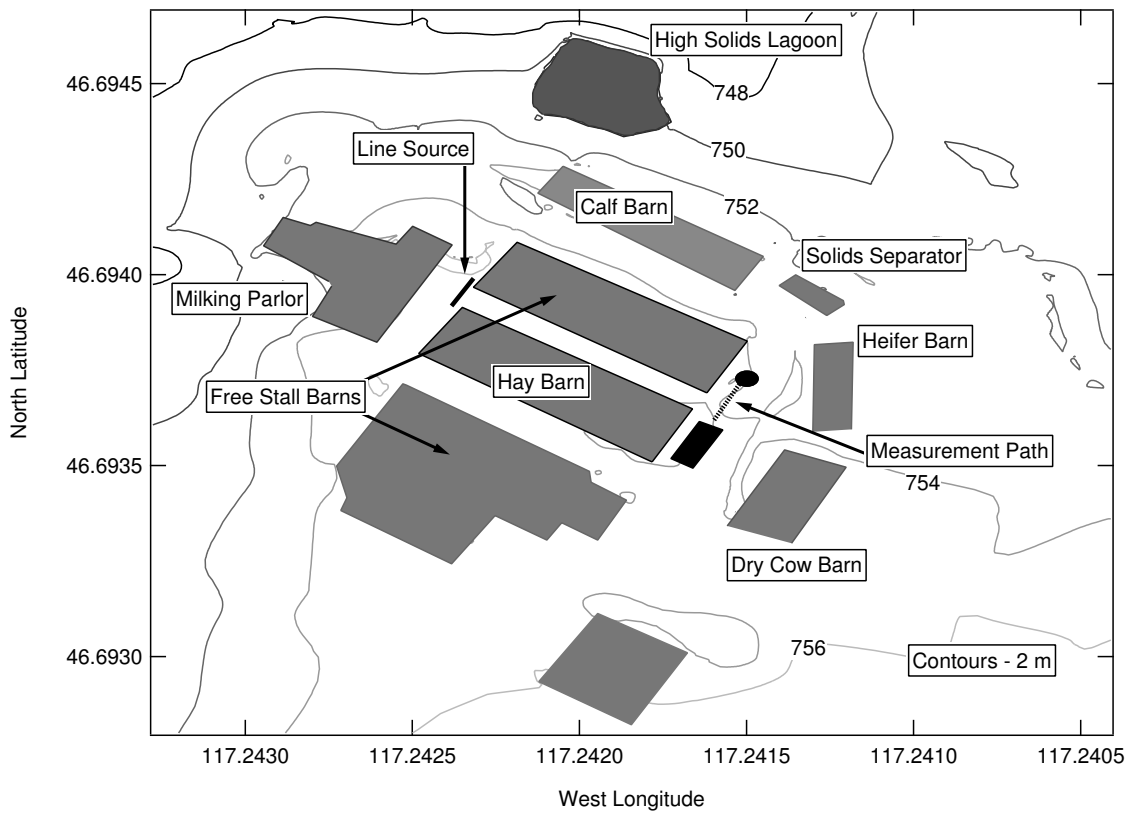


Figure 4.1: WSU Knott Dairy Center milking stalls contour map. Measurements made at the north milking stalls, black rectangle signifies the instrument position and circle signifies the retroreflector mirror position and the dashed line is the measurement path.

stands. The tracer gas was released at the far end of the stalls on the ground.



Figure 4.2: North milking stalls with spectrograph and light source in the trailer, retroreflectors on the right, tracer gas syringe samplers on the stands, during tracer experiment.

4.3.2 Nitrogen Mass Balance

A independent method of calculating stall emissions is to calculate a N mass balance. Cassel et al. (2005b) performed a similar calculation but only for the urea-N as potential for NH_3 emissions. The conversion of organic N from the manure to NH_3 in the waste lagoons was not accounted for. Ammonia is the dominant N volatile species in the stalls, so it was assumed that all N lost was in the form of NH_3 . Due to difficulties in estimating some of the amounts used in the analysis, the error of the mass balance is approximately $\pm 20\%$. The results are shown in Table 4.1 and explained below.

Table 4.1: Nitrogen mass balance for the milking cows and waste treatment system of the WSU Knott Dairy Center. Nitrogen imports are additions to the milking cow stall area or the waste lagoon system and exports are subtractions from the stalls or lagoon system not accounting for volatilization.

Imports	N (kg yr ⁻¹)	N (kg cow ⁻¹ yr ⁻¹)
Feed	51000	290
Bedding	1900	11
New Cows - Heifers	1100	6
Total Imports	54000	310
Exports		
Milk	11500	66
Solids	7700	44
Culled Cows	1100	6
Calves	200	1
Nitrogen in Lagoons	27000	150
Total Exports	20500	120
Maximum Nitrogen Stall Emissions	6500	37

The imports to the milking cow stalls include feed, bedding and new cows. The 175 cows consume 26 kg of feed daily on a dry matter basis. The feed is 19% crude protein. N is calculated by dividing the crude protein by 6.25 (NRC, 2001). This gives an annual milking cow N intake of 51000 kg. Compost is used as bedding at the WSU dairy and is disposed of with the waste, so it has the potential to enter the lagoon system. The dairy uses 666800 kg of compost per year which is 41.2% dry matter, and of that 0.7% is N for a total of 1,900 kg of N. Sixty fresh heifers are added each year and they weigh 600 kg with a body composition of 2.88% N for an import of 1100 kg (Kohn, 2002). Runoff from the dry cow and heifer barns drains into the waste lagoons but the annual N amount is estimated to be less than 100 kg.

Exports from the milking cow stall area and the waste system include milk, waste, calves, and culled cows. The average milk production per year for the entire dairy is 2172300 kg with a milk protein content of 3.30%. The average milk production per cow is 10300 kg year⁻¹. This gives a N milk export of 11500 kg year⁻¹. The N in the waste can either volatilize, be composted or go into the lagoon system. The total solids exported from the dairy is 2880000 kg which is 26.1% dry matter and 1.14% is N. This gives a total N export of solids of 8600 kg with approximately 10% of that coming from the dry cow and heifer barns.

Calves born each year number 175, with an average weight of 41 kg. Sixty milking cows are culled each year with a weight of 635 kg each. Assuming a N body percentage of 2.53% for calves and 2.88% for culled cows the total nitrogen exports are 200 kg N and 1,100 kg N exported for calves and culled cows respectively (Kohn, 2002). The total liquid volume of the lagoons is 29000 m³. Neger (2002) extensively sampled the waste lagoons, the average N concentration was 1025 mg L⁻¹ which gives a total waste N in the lagoons of 30000 kg N with a holdover from the previous year of 2700 kg N. Thus, the total N added during the year is approximately 27000 kg N.

The difference between nitrogen unaccounted for and the amount in the lagoons should be the maximum annual N emitted from the stalls and that is 6500 kg N or 7900 kg NH₃, or 45 kg NH₃ cow⁻¹ yr⁻¹.

4.3.3 Air Analysis

Atmospheric NH₃ concentrations were measured using an open path differential optical absorption spectroscopy (DOAS) method as described by Mount et al. (2002). The instrument measures the photoabsorption of NH₃ in the mid-ultraviolet from 200 to 235 nm. The spectrograph is housed in a trailer along with the Xenon light source, collimating and collecting optics. Retroreflectors were used to direct the light beam to the collecting optics and then into the spectrograph. The spectrograph is a double crossed Czerny-Turner with a silicon array diode detector. The instrument has a very high signal to noise ratio (> 0.02%) allowing high precision measurements as fast as every second. The detection limit is a few ppbv. For the experiment, one second spectra were co-added and recorded approximately every five minutes. The instrument was set up approximately 5 m downwind of the stalls perpendicular to the prevailing wind direction. The total path length was 35 m.

Sulfur hexafluoride (SF₆) was used as a tracer gas due to its low reactivity. The higher molecular weight of SF₆ compared to NH₃ has a negligible effect because turbulent diffusion is the dominant transport mechanism (Kaharabata et al., 2000). The SF₆ was released along

the upwind edge of the milking stalls from a copper line with 4 restrictors spaced every 4 m. Sequential 30 minute samples were collected using syringe samplers placed along the DOAS measurement path. The syringes were taken to the laboratory and within hours analyzed using a HP 5880A gas chromatograph (Hewlett Packard, Palo Alto, CA) with EC detector. Scott-Marrin (Riverside, CA) SF₆ standards with ±5% certified accuracy were used for calibration of the GC. Line source emission rates of SF₆ were measured using an Alltech Digital Flow Check (Alltech, Deerfield, IL) flow meter. A Campbell Scientific Weather Station is located at the north east end of the lagoon. Average wind speed and direction at a height of 3 m were measured every five minutes with a R.M. Young 05103 Wind Monitor. A one sigma wind direction deviation was also calculated for each five minute period. Ambient air temperature and relative humidity were measured with a Campbell Scientific Model HMP35C Probe with a Vaisala capacitive humidity sensor at 2 m height.

4.3.4 Sulfur Hexafluoride Tracer Ratio Technique

An area source tracer ratio technique developed by Ludwig et al., (1983) was used to calculate the flux from the stalls. The tracer gas is released as close as possible upwind of the area source at a known rate, and measured downwind at the same location as the concentration of the pollutant. Knowing the release rate and the downwind concentrations, the pollutant emission rate can be calculated. The technique has been used successfully to measure emissions from various area sources (Lamb et al., 1995; Shorter et al., 1997; Howard et al., 1992; Eklund, 1999). The best conditions for tracer experiments are during a steady wind with good turbulent mixing so that the tracer gas plume thoroughly mixes with the pollutant plume and is transported over the measurement array.

The equation for the concentration downwind of an infinite line source is the following

$$C_l = \frac{2Q_l}{\sigma_z u \sqrt{2\pi}} \quad (4.2)$$

where C_l is the line source concentration at ground level (g m^{-3}), Q_l is line source emission

rate ($\text{g m}^{-1} \text{s}^{-1}$), σ_z is the vertical plume diffusion coefficient, and u is the wind speed (m s^{-1}). Vertical diffusion varies with downwind distance so the following was assumed:

$$\sigma_z = ax^b \quad (4.3)$$

where a and b are empirical coefficients and x is downwind distance (m).

For an area source Equation 4.2 can be integrated to yield:

$$C_A = \frac{2Q_A(X_u^{1-b} - X_d^{1-b})}{ua(1-b)\sqrt{2\pi}} \quad \text{for } b \neq 1 \quad (4.4)$$

where C_A is the concentration at ground level (g m^{-3}), Q_A is the area source emission rate ($\text{g m}^{-2} \text{s}^{-1}$), X_u is the distance to upwind edge of the area source (m) and X_d is the distance to downwind edge of the area source (m).

The area source and line source equations can be combined to solve for the flux from the area source; the only unmeasured variable is b which can be estimated from the tracer measurements or taken from the literature.

$$Q_A = \frac{C_A Q_l (1-b)}{C_l (X_u^{1-b} - X_d^{1-b}) x^b} \quad (4.5)$$

A multiple point source tracer technique was also used to test the line source method. The method, outlined by Kaharabata et al. (2000), was used where a series of point sources were released throughout the cow stalls and then SF_6 was measured along the instrument path. The point source method is advantageous since there is no requirement for atmospheric dispersion variables and the point sources are spread throughout the source area so differences in turbulence in the stalls is taken into account. The equation for the point source flux method is

$$Q_{NH_3} = \frac{Q_{SF_6} C_{NH_3}}{C_{SF_6}} \quad (4.6)$$

where Q is the flux of the gas (g s^{-1}) and C is the concentration (g m^{-3}).

Tracer experiments were only conducted during times of high west winds with small σ_θ to ensure that the north stalls were being measured. During low ambient wind speeds and high σ_θ the wind field in and around the stalls was unpredictable.

4.3.5 Emissions Model

The emissions of NH_3 from the urine puddles to the atmosphere were predicted using two models, a cow model to calculate liquid NH_3 concentrations based upon cow diet and production factors and a mechanistic model of the transport of NH_3 to the bulk atmosphere from the liquid NH_3 . Modeling the release of NH_3 from the stalls is complicated since the emission source (urine puddles), is not uniformly distributed over the entire area. Low spots and areas where the cows congregate have more urine puddles than other areas and old urine puddles have lower NH_3 concentrations due to previous NH_3 emissions. Modeling the urination and reaction of individual urine puddles with the urease was not attempted; instead the stall area was treated as a uniform emission source. The bedding area was excluded since urination and defecation are not common there.

The transfer of NH_3 from the urine puddles to the atmosphere requires that resistances to the liquid and gaseous phases be overcome. The liquid transfer of NH_3 in the urine puddle is by diffusion and the transfer in the atmosphere is dependent upon wind speed and temperature. Mechanistic models have been used to model the release of NH_3 from manure and Ni (1999) has provided a detailed review of mechanistic models and NH_3 releases from animal waste. The mechanistic mass transfer model is given by the following equation

$$q_a = h_m(NH_{3(a,0)} - NH_{3(a,\infty)}) \quad (4.7)$$

where q_a is the flux per unit area ($\text{g m}^{-2} \text{s}^{-1}$), h_m is the convective mass transfer coefficient, $NH_{3(a,0)}$ is the concentration at the air-water interface, and $NH_{3(a,\infty)}$ is the concentration in the free air stream. The h_m depends upon the wind speed, temperature, surface

roughness, air density, and viscosity and is usually determined empirically. The liquid NH_3 concentration depends upon the UUN concentration and the partitioning of ammonia-N as described below. The $\text{NH}_3(a,0)$ depends upon the temperature dependent volatilization rate from the liquid described by the Henry's law constant and the liquid NH_3 concentration. The $\text{NH}_3(a,\infty)$ was assumed to be 0 since upwind measurements were below the detection limit of the instrument of 2 ppbv.

The liquid NH_3 concentration is calculated by first calculating the UUN concentration. The UUN varies depending upon cow parameters and diet. For the WSU dairy the dietary information is known; if dietary information is not known, NRC (2001) lists dietary recommendations that can be used for the calculations.

Calculating the UUN requires some dietary and cow parameters as shown below. The dry matter intake (DMI) needs to be known or can be calculated as shown below. The DMI (kg day^{-1}) is based upon the milk production and the 4% fat corrected milk according to Equation 4.8 reported by NRC (2001)

$$DMI = (0.372 * FCM + 0.0968 * BW^{0.75})(1 - e^{-0.192*(WOL+3.67)}) \quad (4.8)$$

where WOL is the week of lactation (range 1 to 48) and FCM is the 4% fat corrected milk, BW is the body weight (range 600 to 750 kg). For the WSU dairy a WOL of 24 was used and the cows weigh approximately 720 kg. The calculation of the FCM is shown in Equation 4.9.

$$FCM = 0.4 * MP + MF * 15 \quad (4.9)$$

where MP is milk production ($\text{kg cow}^{-1} \text{ day}^{-1}$) and MF is milk fat ($\text{kg cow}^{-1} \text{ day}^{-1}$). Milk production at the WSU dairy is 41 kg day^{-1} , milk fat percent is 3.3% and thus MF is 1.4 kg day^{-1} .

The excretion of N in the urine has been reported to be a function of the intake of N

and milk excretion (Bannink et al., 1999). The digested N (D_N) in $\text{g cow}^{-1} \text{day}^{-1}$ can be calculated according to the following equation

$$D_N = -42.5 + 0.738 * I_N \quad (4.10)$$

where I_N is the N intake (g day^{-1}) which can be calculated by multiplying the crude protein (CP) percentage by the DMI and dividing by 6.25. The recommended levels of CP are between 14% and 19% of DMI, depending upon the cows and diet components (NRC, 2001). Feeding a high protein diet can be cost prohibitive and the NRC, (2001) lists dietary recommended levels of between 14% and 19% of DMI, the WSU feed is 19% CP.

The milk N (M_N) in g day^{-1} can be calculated using the following equation from Bannink et al. (1999).

$$M_N = 46.62 + 3.681 * MP \quad (4.11)$$

Urinary N (UN) in g day^{-1} can be calculated with the following equation from Bannink et al. (1999).

$$U_N = 75.18 + 0.719 * (D_N - M_N) \quad (4.12)$$

The urine volume U_{vol} (kg day^{-1}) is needed to convert the N mass to a concentration; according to Bannink et al. (1999) U_{vol} can be calculated by the following

$$U_{vol} = 0.1153 * I_{Na} + 0.0577 * I_K \quad (4.13)$$

where I_{Na} and I_K are the daily consumption of Na and K (g day^{-1}). The recommended level Na intake is 0.038 times the body weight and for K is $2.6 \text{ g K kg}^{-1} \text{ DMI}$ plus 0.038 times the body weight (NRC, 2001).

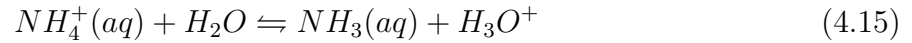
Burgos et al. (2005) found the following linear relationship between the concentration of

UN and UUN from lactating dairy cows.

$$UUN = 0.21 + 0.0065 * UN \quad (4.14)$$

Where UUN and UN concentrations are in $g L^{-1}$. The reaction of UUN with urease is relatively fast, calculation of the reaction rate using a Michaelis-Menten equation from Monteny et al., (1998) showed that the conversion only takes a few minutes. Since the conversion of UUN to ammonia-N is fast and the stalls were treated as an uniform area source all the UUN was converted to ammonia-N.

The NH_3 is in equilibrium with NH_4^+ depending upon the pH of the solution according to the following relationship



The equilibrium between NH_3 and NH_4^+ in solution depends upon the pH of the solution and can be described by the equilibrium constant K_d .

$$K_d = [H_3O^+(aq)] \frac{[NH_3(aq)]}{[NH_4^+(aq)]} \quad (4.16)$$

where [] denotes molar concentrations. The pH of the cow urine is estimated to be between 7 and 8 given the diet. The average lagoon pH was measured to be 7.8 (Neger, 2002); that was used for the model since it is a combination of the urine and manure from the stalls.

Equation 4.17 (Kamin et al., 1979) was used to determine the equilibrium constant.

$$K_d = 10^{-\left(0.09018 + \frac{2729.92}{Temperature(K)}\right)} \quad (4.17)$$

The concentration of NH_3 released to the atmosphere is governed by the following equation.



The Henry's law constant K_H can be used to calculate the partitioning of NH_3 in the gas and liquid phases. Ni (1999) noted that many different forms of Henry's Law have been used to study NH_3 emissions from waste. A non-dimensional form of the Henry's Law equation was used

$$K_H = \frac{NH_3(g)}{NH_3(aq)} \quad (4.19)$$

The equation of Monteny et al. (1996) for NH_3 in water was used to determine the Henry's constant.

$$K_H = 1384 + 1.053^{(293 - Temperature(K))} \quad (4.20)$$

Modeling the excretion of UUN based upon cow parameters allows the model to be adaptable to differing dairy farming practices. The coupling of the cow model and the chemistry between NH_3 and NH_4^+ in solution allows for the model to account for climate and seasonal differences in emissions.

4.4 Results and Discussion

4.4.1 Concentration Measurements

Figure 4.3 shows measured atmospheric NH_3 concentration data averaged over approximately every two minutes with wind speed and wind direction averaged over 10 minutes on September 16, 2004. As expected the NH_3 concentrations were the lowest when the wind speeds were the greatest and varied when the wind direction was changing. The highest concentration measured at the stalls was 2500 ppbv during the summer during low wind conditions. The lowest concentration measured was 300 ppbv during the winter.

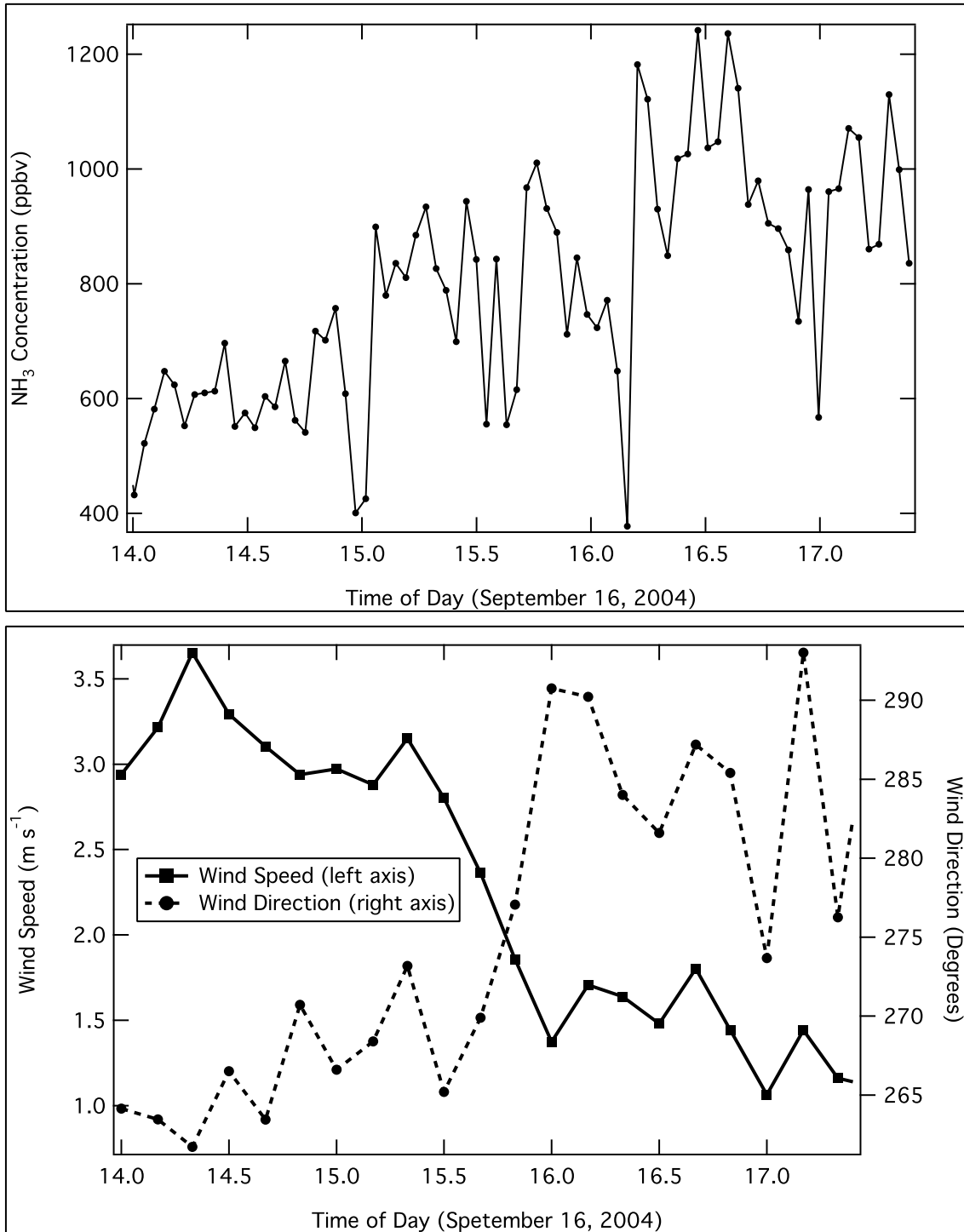


Figure 4.3: Ammonia concentrations (upper panel) averaged over approximately 2 minutes and wind speed and direction (lower panel) averaged over 10 minutes showing the the relationship between wind speed and direction and NH₃ concentrations.

Figure 4.4 shows the NH_3 concentration measured every minute on July 23, 2003 and the large degree of fluctuations demonstrating the turbulent mixing in the stalls. Smoke release experiments were conducted in the stalls and they also showed large vertical mixing. The vertical mixing was the greatest by the line source due to the building wake from the milking parlor and decreased towards the instrument path.

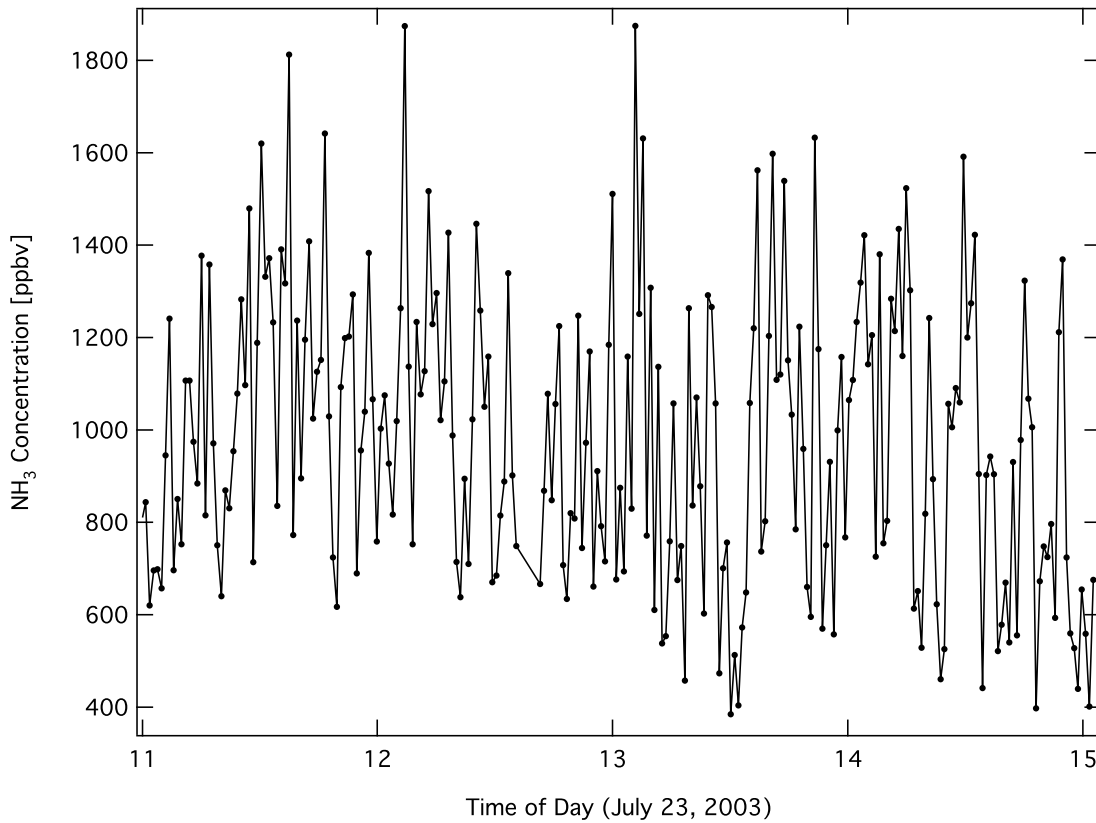


Figure 4.4: Ammonia concentrations (ppbv) for July 23, 2003. Measurements averaged every minute demonstrate the turbulence in the stalls.

4.4.2 Tracer Ratio Experiments

The line source emission and tracer concentration data were used in Equation 4.2 with σ_z calculated using Equation 4.3 to evaluate the literature variables of a and b of Busse and Zimmerman (1973). The plume model over estimated the concentration so a virtual area source emission method was then used to simulate the enhanced vertical dispersion. The virtual emission source method accounts for the increased vertical dispersion by creating

a virtual source upwind of the actual source so it is possible to apply normal dispersion variables at the source. The virtual source distance was calculated by using tracer and sonic anemometer data in Equation 4.21:

$$\sigma_z = \frac{\sigma_w x_v}{u} \quad \text{or} \quad x_v = \frac{\sigma_z u}{\sigma_w} \quad (4.21)$$

where x_v is the virtual distance of the source (m), σ_w was measured using the sonic anemometer, and σ_z was calculated from the tracer emissions and concentration data. The calculated x_v ranged from 72 to 898 m; outliers were removed and an average of x_v of 356 m was calculated. The line source data were again used to evaluate x_v using Equations 4.2 and 4.3 with the literature values of a and b based upon stability. The plume model over predicted concentrations so new values of a and b were calculated.

New wind speed dependent a and b variables were calculated by plotting wind speed against σ_z , σ_z from the line source emission and concentration data. Average values of σ_z were obtained for each 1 m s⁻¹ change in wind speed. Wind speed dependent σ_z values were calculated by linearly interpolating between the values of a and b given by Busse and Zimmerman (1973) and then calculating σ_z , a and b values that corresponded to the wind speed σ_z values were then used. The new variables showed good agreement with the line source tracer data.

The average NH₃ flux from the line source tests was 740 ± 470 μg m⁻² s⁻¹ ± at an average temperature of 18° C. The large variation is due to turbulence in the stalls and temperature differences over the various experiments. Figure 4.5 shows representative results of a tracer experiment on September 16, 2004 along with the concentration of NH₃ and SF₆ and wind speed. The NH₃ and SF₆ concentrations track each other and increase with decreasing wind speed. The average NH₃ flux from the point source experiment was 420 μg m⁻² s⁻¹ ±110 μg m⁻² s⁻¹ at a temperature of 14° C.

During the point source experiment samplers were set out to the north and south of the measurement path to determine the plume size. The instrument path measured about

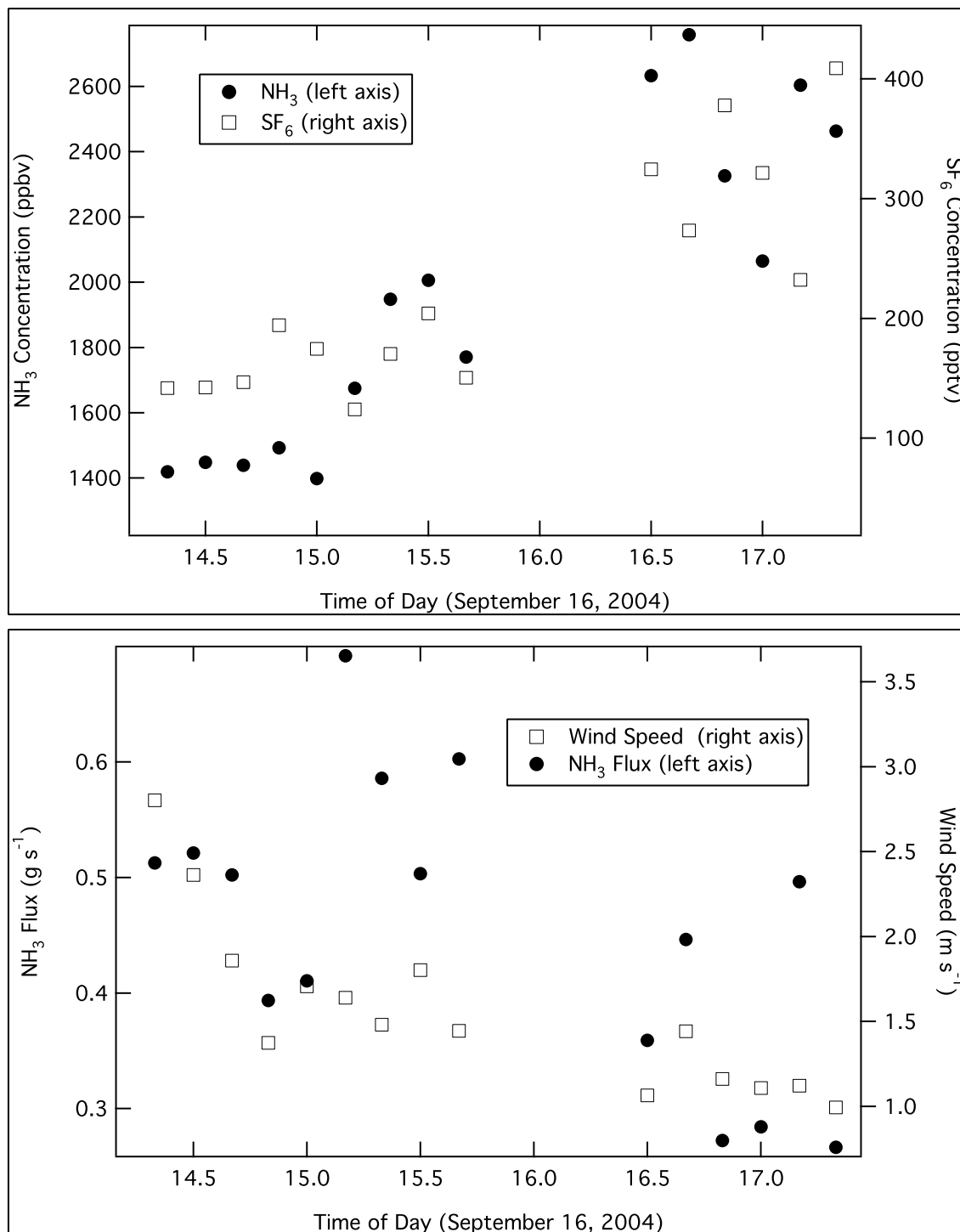


Figure 4.5: Point source tracer experiment, NH₃ and SF₆ concentrations on the top panel and wind speed and NH₃ flux on the bottom panel.

50% of the plume for the given wind conditions. Since both the line source method and the multiple point source method are ratio methods it is not necessary to measure the entire plume. When using the line source tracer ratio method Ludwig et al. (1983) suggested using the highest downwind concentration since that point best approximates the Gaussian plume line source equation. Assuming the NH₃ from the south stalls behaves as the north stalls does, some of the NH₃ measured is from the south stalls. This would lead to an over prediction of emissions, but given the turbulence, it is difficult to quantify the error. The N mass balance gives an independent check of maximum housing emissions.

4.4.3 Emissions Model

The mechanistic and plume models were then used to model downwind measured concentrations and compared to measured concentration to determine model error. The value of h_m was empirically fit to the data and determined to be 3.8×10^{-3} . Figure 4.6 shows the modeled and measured half-hour averaged concentrations, and the scatter about the 1:1 line. Overall the model and the measurements show the same trend. The normalized mean error of the model was 30%. The model tended to underpredict NH₃ concentrations as shown in the first row of Table 4.2.

4.4.4 Modeling Sensitivity Analysis

A sensitivity analysis of the model input parameters was conducted and results compared to measured NH₃ concentrations. The statistics to evaluate the models were the mean bias (MB), normalized mean bias (NMB), and normalized mean error (NME) as given by the following equations.

$$MB = \frac{1}{n} \sum (X_{mod} - X_{meas}) \quad (4.22)$$

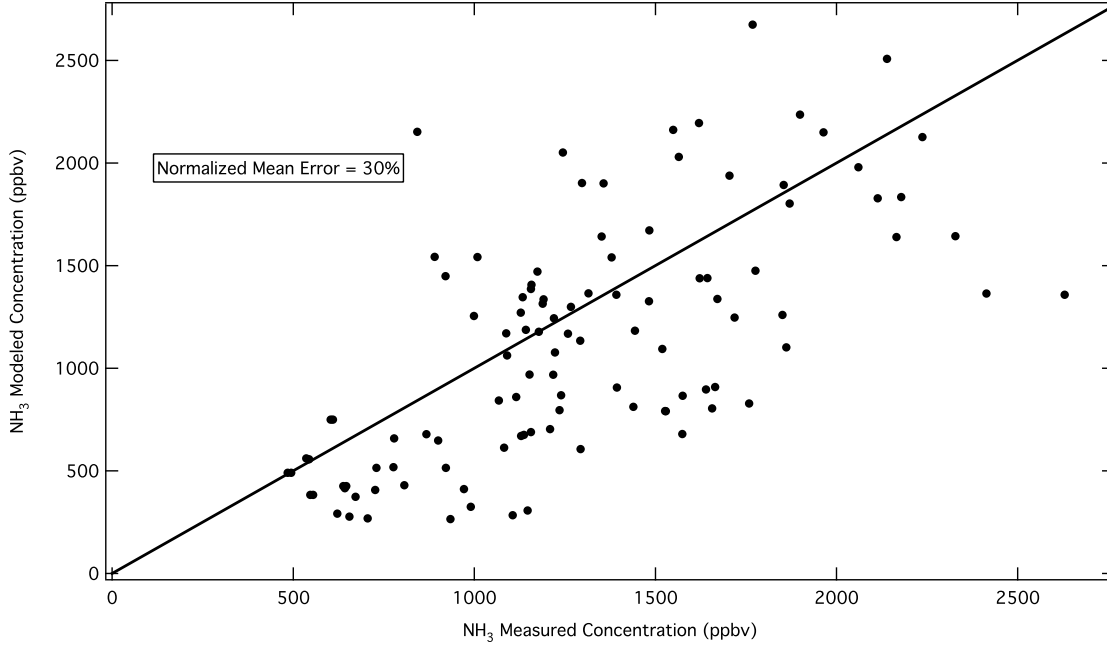


Figure 4.6: Half-hour averaged measured and modeled NH_3 concentrations (ppbv) from the milking stalls from 2001 to 2004. Solid line is the 1:1 line.

$$NMB = \frac{\frac{1}{n} \sum_1^n (X_{mod} - X_{meas})}{\frac{1}{n} \sum_1^n X_{meas}} 100\%. \quad (4.23)$$

$$NME = \frac{\sum_1^n |X_{mod} - X_{meas}|}{\sum_1^n X_{meas}} 100\%. \quad (4.24)$$

Where n is the number of data points, X_{mod} is the modeled concentration and X_{meas} is the measured concentration.

Table 4.2 shows the sensitivity analysis results of the emissions and plume model compared to the measured concentrations and the average model calculated flux and the flux standard deviation. For the base case, milk production was $41 \text{ kg cow}^{-1} \text{ day}^{-1}$, crude protein was 19%, air temperature was used as urine puddle temperature, and the pH was 7.8. For the base case the model under predicts the concentration as indicated by the NMB of -12%. The model was most sensitive to changes in the pH. Increasing the pH resulted in

Table 4.2: Housing emissions sensitivity analysis of measured NH_3 concentrations versus downwind modeled concentrations for 110 half-hour average time periods. Sensitivity statistics: mean bias (MB), normalized mean bias (NMB), normalized mean error (NME) and average flux. Average model flux and standard deviation for the time periods.

Model Base Case Deviation	MB (ppbv)	NMB (%)	NME (%)	Average Flux ($\text{mg cow}^{-1} \text{s}^{-1}$)	Flux Std. Dev. ($\text{mg cow}^{-1} \text{s}^{-1}$)
Base Case	-150	-12	30	5.5	2.1
pH = 8.1	930	72	76	10	4.0
pH = 7.9	130	0.097	35	6.7	2.6
pH = 7.7	-380	-30	35	4.3	1.7
pH = 7.5	-710	-55	56	2.7	1.1
Temperature + 5° C	320	25	41	7.6	2.8
Temperature + 2° C	10	0.82	31	6.1	2.3
Temperature - 2° C	-320	-25	32	4.6	1.8
Temperature - 5° C	-510	-40	42	3.7	1.5
Milk Production = 50 kg day^{-1}	80	6.2	33	6.5	2.5
Milk Production = 45 kg day^{-1}	-49	-3.8	31	5.8	2.3
Milk Production = 35 kg day^{-1}	-310	-24	32	4.6	1.8
Milk Production = 30 kg day^{-1}	-435	-34	37	4.0	1.6
Crude Protein = 21%	-19	-19	31	6.0	2.3
Crude Protein = 17%	-280	-22	31	4.7	1.8
Crude Protein = 15%	-420	-32	36	4.1	1.6
h_m + 25%	130	10	35	6.8	2.7
h_m + 10%	-38	-3.0	31	6.0	2.3
h_m - 10%	-270	-21	31	4.9	1.9
h_m - 25%	-440	-34	37	4.1	1.9

over predicting concentrations and also resulted in much higher average fluxes along with larger flux standard deviations. The model actually did better than the base case when the temperature was +2° C over ambient. This is probably due to solar radiation warming the concrete urine puddles above ambient air temperatures. Increasing the milk production to 45 or 50 kg day^{-1} reduces the bias in the model, but does not improve the NME. Underestimating milk production results in the model under predicting the concentration. Increasing the crude protein intake to 21% also reduces the bias, but does not improve the NME.

4.4.5 Annual Emissions

The theoretical model was run for a year to understand the seasonal variation of emissions and to validate the model with the annual N balance. The weather data were taken from the WSU campus on top of a building approximately 8 km from the dairy. Fluxes were calculated for meteorological data with a wind speeds above 1 m s^{-1} ; below that wind speed it was assumed that the wind speed at the surface was 0 so the transfer to the bulk atmosphere was 0. Figure 4.7 shows the daily emissions for 2001 along with the daily average temperature. The large variation during the warm part of the year is due to low wind speeds typical of summer conditions. The modeled total annual emissions from the stalls is 7000 kg ($40 \text{ kg NH}_3 \text{ cow}^{-1}$) which is in good agreement with the dairy mass balance of 7900 kg.

4.5 Approximate Error Analysis

The error in the tracer ratio method can be estimated through a propagation of error analysis. The error in the measurement of the SF_6 emission rate is derived from changes in the flow from the line source due to heating and cooling and errors in measuring the flow. Duplicate flow measurements gives an error of $\pm 5\%$ and multiple measurements of the flow shows an agreement to within $\pm 2\%$. The combination of these two uncertainties gives the error from the tracer release rate of $\pm 7\%$. The error in the measurement of the SF_6 is due to calibration errors and the precision of the measurement. The calibration gases have an accuracy of $\pm 5\%$ and the precision of the measurements is about $\pm 5\%$ for a total error in the SF_6 measurement of $\pm 7\%$.

The uncertainty in the measurement of NH_3 is derived from errors in the NH_3 ultraviolet absorption cross section due to uncertainties in the concentration of the calibration gas. There are also errors in the measurement of the path length, illumination of the spectrograph, shifts and stretches in the spectra due to thermal changes in the spectrograph and mathematical errors in the retrieval of the concentration. The overall error is estimated to

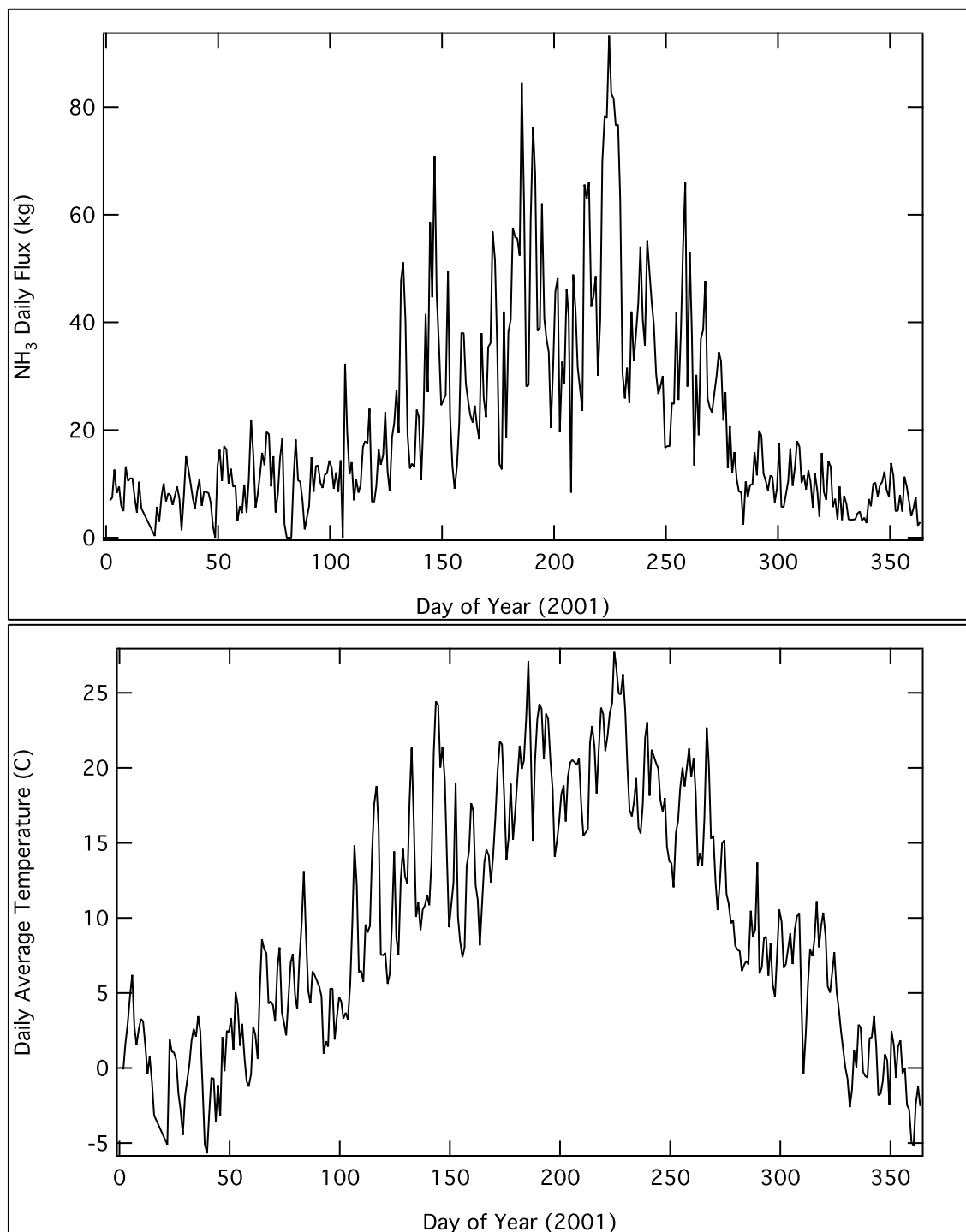


Figure 4.7: Daily model predicted NH₃ emissions from the milking stalls (top panel) and daily average temperature (bottom panel). Wind speed and direction measured near the NH₃ path and the SF₆ syringe samplers.

be $\pm 25\%$ (Mount et al., 2002). Lamb et al. (1995) noted that the error in the dispersion coefficient b is due to uncertainties in the power law estimation of vertical dispersion. The use of experimentally derived values reduced the calculated flux by approximately 20%. Thus, the quantifiable error in NH_3 emission flux based on tracer release errors, model errors and concentration errors for the tracer experiment is $\pm 33\%$.

There are a number of systematic unquantifiable errors in the experiment. The tracer flux equation assumes a rectangular area source and uniform emissions. As discussed above the emissions from the urine puddles are not uniform. Inside the open barn where there are stalls and alleys the airflow is much different from the area between the stall barn and the hay barn. Due to the turbulence, some NH_3 from the south milking stalls was measured but quantification is difficult. A conservative estimate is $\pm 20\%$.

We estimate the overall error at $\pm 40\%$. Data analysis suggests that the overall error is high. However, the agreement of annual emissions with the N mass balance to within -11% shows that the emissions model provides a good estimate of NH_3 emissions. The overall model error compared to measured concentrations is $\pm 30\%$.

4.6 Conclusions

Concentrations of NH_3 were measured downwind of milking dairy stalls using DOAS and fluxes were measured using two area source tracer ratio techniques. The average flux using a line source techniques was $8.1 \pm 5.2 \text{ mg cow}^{-1} \text{ s}^{-1}$ at an average temperature of 18° C . The average flux derived from a point source tracer was $4.6 \pm 1.2 \text{ mg m}^{-2} \text{ s}^{-1}$ at an average temperature of 14° C .

Cow N excretions were modeled based upon cow characteristics and dietary intake. The release of NH_3 to the atmosphere was modeled using a mechanistic model of chemical and physical conditions and a Gaussian plume model calibrated with the tracer data. The model had a normalized mean error of 30% when compared to measured concentrations. The model was very sensitive to changes in the pH and less sensitive to temperature. The model was

not that sensitive to changes in crude protein or milk production. The emission model was run for a year and annual emissions were calculated to be 7000 kg NH₃ (40 kg cow⁻¹ yr⁻¹), in excellent agreement with the N mass balance maximum of 7900 kg. Emissions for the entire dairy of 175 milking cows were seasonal and ranged from about 10 kg NH₃ day⁻¹ in the winter to over 80 kg NH₃ day⁻¹ in the summer.

Chapter 5

Lagoon Emissions

Atmospheric Flux of Ammonia from an Anaerobic Dairy Waste Lagoon

Brian Rumburg, George H. Mount, David Yonge, Brian Lamb, Hal Westberg, Manjit
Neger, Jenny Filipy

Department of Civil and Environmental Engineering

Ron Kincaid, Kristen Johnson

Department of Animal Sciences

Washington State University

Pullman, Washington 99164-2910

to be submitted to

Atmospheric Environment

5.1 Abstract

Atmospheric anthropogenic ammonia (NH_3) emissions are not well understood in the U.S. due to a lack of measurement data from the main emission sources. This paper describes concentration measurements downwind of an anaerobic dairy waste lagoon using differential optical absorption spectroscopy (DOAS), tracer ratio flux experiments and development of a lagoon emissions model. The tracer ratio method involves releasing a measured flux of a tracer gas upwind of the lagoon and measuring the concentration downwind along with the DOAS NH_3 measurement. The flux is calculated by ratioing the tracer flux and concentration with the NH_3 concentration and taking into account the differences in area and dispersion over the area source. Measured fluxes from the tracer experiments ranged from $30 \mu\text{g m}^{-2} \text{s}^{-1}$ at an air temperature of 11°C to $150 \mu\text{g m}^{-2} \text{s}^{-1}$ at an air temperature of 27°C . The NH_3 emissions model was based upon the temperature dependent biological activity, the partitioning of NH_3 and NH_4^+ in solution, and the partitioning of NH_3 between the gas and liquid phases. Comparing measured downwind NH_3 concentrations and modeled concentrations the model had a normalized mean error of 21%. The model was most sensitive to changes in lagoon pH. Emissions were temperature dependent. Annual emissions were $55 \text{ kg NH}_3 \text{ cow}^{-1} \text{ year}^{-1}$ from all lagoons. Using literature lagoon design criteria to estimate lagoon size resulted in an underestimation of emissions of -29%.

5.2 Introduction

The complex impacts of anthropogenic atmospheric ammonia (NH_3) emissions on the atmosphere and the environment are not fully understood due in part to a lack of measurement data and time resolved emission algorithms. Measuring NH_3 is difficult due to its absorptive properties. The lack of measured NH_3 emissions data in the U.S. has led to large uncertainties in estimated emission rates and the factors that influence emission rates, thus making regulation and mitigation difficult (NRC, 2003). NRC, 2003 listed NH_3 as the most impor-

tant atmospheric gas emitted from animal feeding operations in the U.S. due to impacts from deposition and haze. In the atmosphere, NH_3 primarily reacts to form ammonium sulfate and ammonium nitrate aerosols which are regulated as part of the U.S. Environmental Protection Agency National Ambient Air Quality Standards $\text{PM}_{2.5}$ (particulate with an aerodynamic diameter less than 2.5 microns). Ammonia emissions are important due to their $\text{PM}_{2.5}$ precursor status. The main removal mechanism for NH_3 is deposition that can lead to eutrophication of both terrestrial and aquatic ecosystems. The impacts of anthropogenic emissions of NH_3 and other N species on the environment are complex due to the many reaction pathways (Galloway, 1998; Vitousek et al., 1997).

Current global atmospheric emissions of $\text{NH}_3\text{-N}$ are estimated in the range of 45 to 54 Tg N yr^{-1} (Dentener and Crutzen, 1994; vanAardenne et al., 2001; Bouwman et al., 1997). Emissions from agriculture are estimated to be 79% of the global total and almost half of the emissions are from animals (vanAardenne et al., 2001). Domesticated animals produce NH_3 via the reaction of urea in the urine with urease in the soil or in manure and the biological anaerobic breakdown of organic N in the waste. Milking dairy cows have the largest estimated emissions per animal due to the energy required for milk production. Volatilization from anaerobic waste lagoons is one of the sources of NH_3 emissions from dairies. Anaerobic lagoons are commonly used for waste treatment because they have the following advantages: low cost, minimal maintenance, no energy required, and the waste can be used as fertilizer.

The amount of ammonia-N (NH_3 and NH_4^+) in a slurry lagoon depends upon the amount of ammonia-N entering the system, the volatilization rate, and the bacterial breakdown of organic N. Ammonification is the process where bacteria consume soluble organic N and produce ammonia-N. The rate of ammonification is complicated by the fact that the bacteria are also consuming ammonia-N and little research has been done in investigating the rate of ammonification (Grady et al., 1999). Most studies of anaerobic lagoons have looked at the rate of methane production for energy usage and not the rate of ammonification. The rate of bacterial gas production in anaerobic lagoons has been shown to be very low

at temperatures below 15° C and to increase with increasing temperature (Oswald, 1968). Anaerobic lagoons operate best at temperatures above 15° C; at lower temperatures the anaerobic bacteria are not able to metabolize the waste so there is no breakdown of the organic material Middlebrooks et al., 1982; Gray, 2004).

Anaerobic swine lagoon emissions have been studied more extensively than emissions from dairy lagoons. Swine lagoon emissions were estimated to be approximately 33% of total NH₃ swine operation emissions for North Carolina (Aneja et al., 2000). A study of swine lagoons showed that as much as 65% of the N in the lagoon can volatilize as NH₃ (Koelliker and Miner, 1973). Measured swine slurry emissions ranged from 6 to 52 $\mu\text{g m}^{-2} \text{s}^{-1}$ with the highest emissions correlating to the warmest air temperatures (Dore et al., 2004). Aneja et al., 2000 reported a correlation of NH₃ emission fluxes with temperature for swine lagoons: NH₃ fluxes ranged from 81 $\mu\text{g m}^{-2} \text{s}^{-1}$ in the summer to 6 $\mu\text{g m}^{-2} \text{s}^{-1}$ during the winter. An annual average flux of 14 $\mu\text{g m}^{-2} \text{s}^{-1}$ was measured from swine lagoons and emissions were highly correlated with wind speed and water temperatures (Harper et al., 2000). A passive flux sampler was used to measure the flux from a tank with digested animal slurry; there were no emissions at subzero temperatures or slurry covered with straw (Sommer, 1997).

Swine lagoon NH₃ emissions measured with a dynamic chamber were correlated with lagoon temperature and ammonia-N concentration in an empirical emissions model. Emissions ranged from 2 $\mu\text{g m}^{-2} \text{s}^{-1}$ to 0.8 $\mu\text{g m}^{-2} \text{s}^{-1}$ (Aneja et al., 2001a). A process model was developed to simulate emissions from swine lagoons and it explained 50% of the variability of measured data using 4-hour average data (DeVisscher et al., 2002). A model of NH₃ emissions from swine lagoons showed an exponential increase in NH₃ flux with lagoon temperature and pH and a linear relationship between emissions and total ammoniacal nitrogen (Aneja et al., 2001b).

Emission factors for UK dairy slurry lagoons without a cover were 5.3 g NH₃ animal⁻¹ day⁻¹ (Misselbrook et al., 2000). An emission rate of 62 $\mu\text{g m}^{-2} \text{s}^{-1}$ was measured from

Danish dairy slurry lagoons (Sommer et al., 1993). A crust forming over dairy slurry stores was found to reduce NH_3 emissions by 50% (Misselbrook et al., 2005).

This work is part of a study of the emissions of NH_3 from the milking cows at the Washington State University (WSU) dairy. The purpose is to determine the total NH_3 emissions and the factors influencing emissions. The resulting emission algorithms are being used in a regional air quality model. The other sources being measured include the milking cow stalls (Rumburg et al., 2006a) and sprinkler application of wastewater (Rumburg et al., 2005). The objectives were to measure the NH_3 emissions from the lagoon and develop emission algorithms. A theoretical model of lagoon NH_3 emissions was developed and compared to measured concentrations and model sensitivity analysis was conducted. This paper discusses the measurement of emissions from a dairy waste lagoon and the development of the emission model.

5.3 Experimental

Concentration measurements and tracer ratio experiments were made downwind of lagoon 2 from 2000 to 2003. The instrument was located 50 m downwind of the lagoon to ensure the plume was well mixed. Area source tracer ratio experiments were used to determine initial fluxes from the lagoon and to calibrate a Gaussian plume model which was used to determine fluxes when tracer experiments were not being conducted. In addition to atmospheric NH_3 measurements, the slurry lagoon was extensively sampled for N species during late 2000 to early 2002. Meteorological data for the experiments were measured at the north east edge of the lagoon.

5.3.1 Dairy Information

The WSU dairy is located 8 km south of Pullman, Washington USA (N $46^\circ 43.8'$, W $117^\circ 10.1'$). It has approximately 175 Holstein milking cows that contribute to the waste lagoon system. The milking cows are fed a diet of 26 kg of feed per day on a dry matter basis,

the feed crude protein is 19% and milk production averages 41 kg day⁻¹. A schematic and elevation contour map of the dairy is shown in Figure 5.1. The milking cows are housed in three-sided freestall barns with concrete floors. The waste is scraped into waste pits at the south-east side of the stalls daily. The pits are flushed with recycled wastewater from lagoon 2. From the pits, the waste is transported to the solids separator where solids greater than 0.3 cm in diameter are removed. From the solids separator, the remaining waste is gravity fed to lagoon 1. Lagoon 1 is a high solids settling lagoon where additional solids are removed via gravity settling. The supernatant from lagoon 1 flows to lagoon 2. Lagoons 3 and 4 are used for long term storage when lagoon 2 is full. The WSU dairy lagoons are emptied in the late summer and fall. A more complete description of the lagoons and the N and solids contents can be found in Neger (2002) and Rumburg et al., (2004).

5.3.2 Liquid Analysis

Liquid slurry from the lagoon was sampled from November 2000 to April 2002 (Neger, 2002). Ammonia-N was analyzed using distillation and titration methods outlined in sections 4500-NH₃ B and 4500-NH₃ E of *Standard Methods for the Examination of Waters and Wastewaters* (APHA, 1992).

5.3.3 Air Analysis

Atmospheric NH₃ was measured using an open path differential optical absorption spectroscopy (DOAS) method as described in Mount et al. 2002. The open path method is advantageous because it does not suffer measurement problems due to NH₃ adhering to inlet walls. The instrument measures the photoabsorption of NH₃ in the mid-ultraviolet from 200 to 235 nm. The spectrograph is housed in a trailer along with the Xenon light source, collimating and collecting optics. Retro reflectors were used to direct the light beam to the collecting optics and then into the spectrograph. The spectrograph is a double crossed Czerny-Turner design with a silicon array diode detector. The instrument has a very high

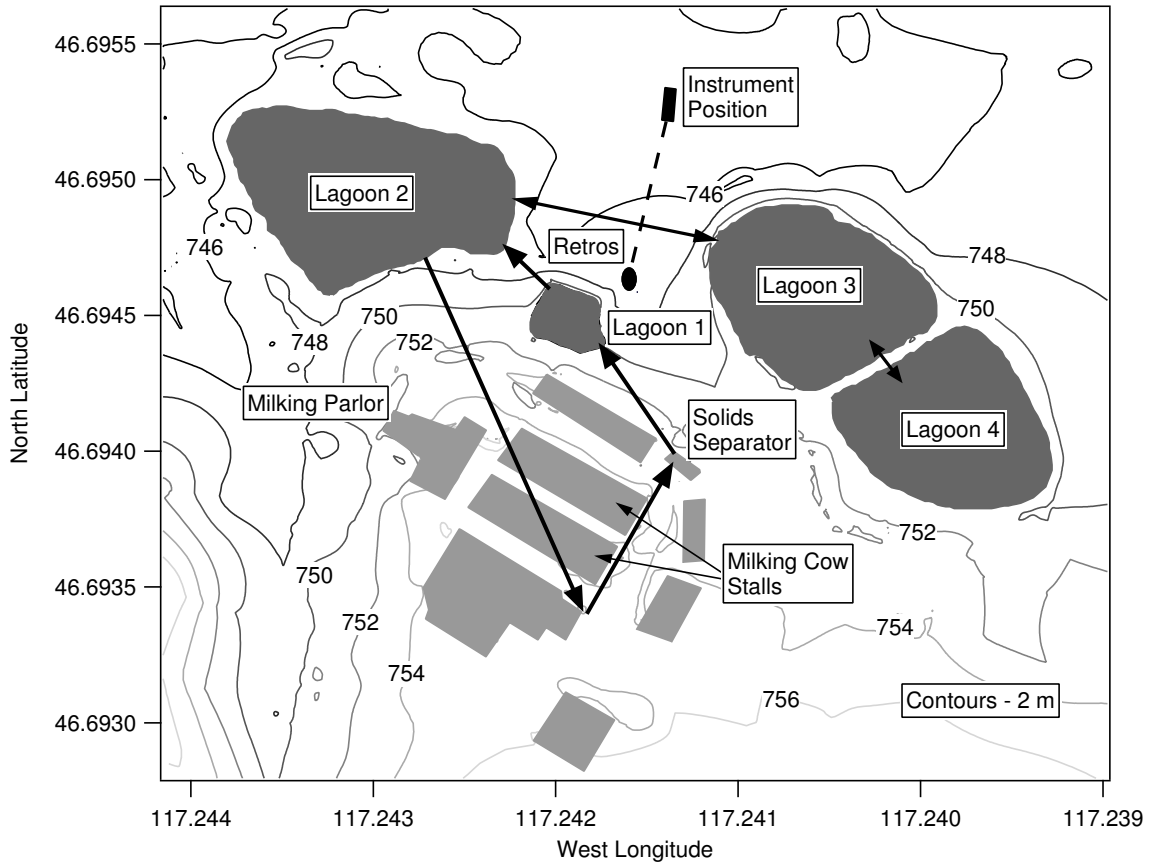


Figure 5.1: WSU Knott Dairy Center contour map. Arrows represent slurry flow between lagoons and stalls and solids separator. Instrument position and retroreflector mirror location designating the instrument path (dashed line) is shown to the left of lagoon 2. Elevation contours are in m. Wind typically is out of the west.

signal to noise ratio allowing high precision measurements as fast as every second. The detection limit is a few ppbv. For the experiment, spectra were co-added and recorded approximately every five minutes. The instrument was set up approximately 50 m east of lagoon 2 with a total path length of 130 m as shown in Figure 5.1.

Sulfur hexafluoride (SF_6) was used as a tracer gas due to its low reactivity. The higher molecular weight of SF_6 compared to NH_3 has a negligible effect due to turbulent diffusion being the dominant transport mechanism (Kaharabata et al., 2000). The SF_6 line source was a 96 m long copper tube with restrictors every 4 m and it was placed on the west edge of lagoon 2. Sequential 30 minute average portable syringe samplers were placed along the instrument path. The syringes were analyzed using a HP 5880A gas chromatograph (Hewlett Packard, Palo Alto, CA), with standards from Scott-Marrin (Riverside, CA). Line source emission rates were measured using a Alltech Digital Flow Check (Alltech, Deerfield, IL) flow meter.

5.3.4 Sulfur Hexafluoride Tracer Ratio Technique

An area source tracer ratio technique first discussed by Ludwig et al. (1983) was used to calculate the flux of NH_3 from the lagoon 2 surface. In this approach, a tracer is released as close as possible upwind of the area source, at a known rate and is measured downwind at the same location as the pollutant concentration from the area source. Knowing the tracer release rate and downwind concentrations it is possible to calculate the pollutant emission rate. The best conditions for tracer experiments are a steady wind so turbulence is the dominant dispersion mechanism and small σ_θ so the tracer plume traverses the area source. The method has been used to measure emissions of natural gas from urban areas (Lamb et al., 1995; Shorter et al., 1997), hydrocarbons from refinery waste impoundments (Howard et al., 1992), and greenhouse gases from cattle processing waste lagoons (Eklund, 1999). Tracer techniques have been shown to be in good agreement with other flux measurement techniques (Lamb et al., 1986).

The equation for the concentration downwind of an infinite line source is the following

$$C_l = \frac{2Q_l}{\sigma_z u \sqrt{2\pi}} \quad (5.1)$$

where C_l is the line source concentration at ground level (g m^{-3}), Q_l is line source emission rate ($\text{g m}^{-1} \text{s}^{-1}$), σ_z is the vertical plume diffusion coefficient, and u is the wind speed (m s^{-1}). For this derivation the following assumption was made

$$\sigma_z = ax^b \quad (5.2)$$

where a and b are empirical coefficients and x is the distance of the emission source from the receptor.

For an area source the above equation can be integrated to yield:

$$C_A = \frac{2Q_A(X_u^{1-b} - X_d^{1-b})}{ua(1-b)\sqrt{2\pi}} \quad \text{for } b \neq 1 \quad (5.3)$$

where C_A is the area source concentration at ground level (g m^{-3}), Q_A is the area source emission rate ($\text{g m}^{-2} \text{s}^{-1}$), X_u is the distance to upwind edge of area source (m) and X_d is the distance to downwind edge of area source (m).

The area source and line source equations can be combined to solve for the flux from the area source. The only unmeasured variable is b which can be estimated from the tracer measurements or taken from the literature.

$$Q_A = \frac{C_A Q_l (1-b)}{C_l (X_u^{1-b} - X_d^{1-b}) x^b} \quad (5.4)$$

Tracer experiments were conducted during periods of high west winds to ensure that SF_6 and the NH_3 plume from the lagoon was being measured. During low wind speeds and times of high σ_θ the SF_6 and NH_3 plumes separated and the results were inconsistent.

5.3.5 Theoretical Model

A mechanistic model was used to determine the relationship between the chemical and physical lagoon characteristics and NH_3 emissions. The concentration of ammonia-N in the lagoon is a function of the amount of ammonia-N entering the lagoon, biological breakdown of the organic N to ammonia-N, and NH_3 emissions. It was assumed that the amount of N entering the lagoon was constant because the number of cows and their diet did not change. The biological breakdown rate in the lagoon is seasonal as shown by the top panel of Figure 5.2. The drop in ammonia-N concentrations during the summer of 2001 is due to slurry from lower ammonia-N concentration waste from lagoons 3 and 4 being drained into lagoons 2 to conduct an aeration experiment (Rumburg et al., 2004). A correction for the dilution was made based upon ammonia-N concentrations from lagoons 3 and 4 and estimated volumetric contributions from both lagoons. The decrease in concentration following July 1, 2001 in the graph is due to the error in the dilution correction. The lower panel of Figure 5.2 shows the concentration of ammonia-N as a function of temperature (round dots) on the left axis as well as the expected NH_3 flux based upon the lagoon pH and temperature (squares) on the right axis. The high ammonia-N concentration at -2°C is most likely a sampling error. Pole sampling from the edge of the lagoon was used to sample during that time and it is likely that a non-representative amount of lagoon solids were collected, increasing the ammonia-N concentration.

According to Grady et al. 1999 the modeling of ammonification can be expressed as a function of a reaction rate for soluble organic-N, an ammonification rate constant, the soluble organic-N concentration, and the active heterotrophic biomass concentration. The effects of temperature on the rate constant over the range of temperatures in which bacteria grow can be expressed as a lognormal function. The data show an increase in ammonia-N concentration above 8°C ; unfortunately there are not enough data to determine the rate of ammonia-N production in the lagoon from 8°C to 12°C or the shape of the function. The rate of volatilization from the lagoon is relatively constant over the 0°C to 10°C range

as shown in the lower panel of Figure 5.2. The rate of volatilization increases more rapidly above 12° C and the concentration in the lagoon remains relatively constant. Due to the lack of data, a step function was used for the concentration in the lagoons. Below 10° C the lagoon ammonia-N concentration was set at 530 mg L⁻¹ and above 10° C it was set at 660 mg L⁻¹.

The transfer of NH₃ from the lagoon to the atmosphere requires that resistances to the liquid and gaseous phases be overcome. The liquid transfer of NH₃ in the lagoon is by diffusion and the transfer in the atmosphere is dependent upon wind speed and temperature. Mechanistic models have been used to model the release of NH₃ from manure and Ni (1999) has a detailed review of mechanistic models and NH₃ releases from animal waste. The convective mass transfer from the liquid to the atmosphere can be modeled by a mechanistic model. The mechanistic model is described by the following equation

$$q_a = h_m(NH_{3(a,0)} - NH_{3(a,\infty)}) \quad (5.5)$$

where q_a is the flux per unit area (g m⁻² s⁻¹), h_m is the convective mass transfer coefficient, $NH_{3a,0}$ is the air concentration at the liquid-air interface, and $NH_{3a,\infty}$ is the concentration in the free air stream both in units of g m⁻³. The h_m depends upon the wind speed, temperature, surface roughness, air density and viscosity and is usually determined empirically. The liquid NH₃ concentration depends upon the partitioning of liquid NH₃ and NH₄⁺ as described below and the concentration of ammonia-N in solution. The $NH_{3(a,0)}$ depends upon the temperature dependent volatilization rate from the liquid described by the Henry's law constant and the liquid NH₃ concentration. The $NH_{3(a,\infty)}$ was assumed to be 0 since upwind measurements were below the detection limit of the instrument.

The NH₃ is in equilibrium with NH₄⁺ depending upon the pH of the solution according to the following relationship



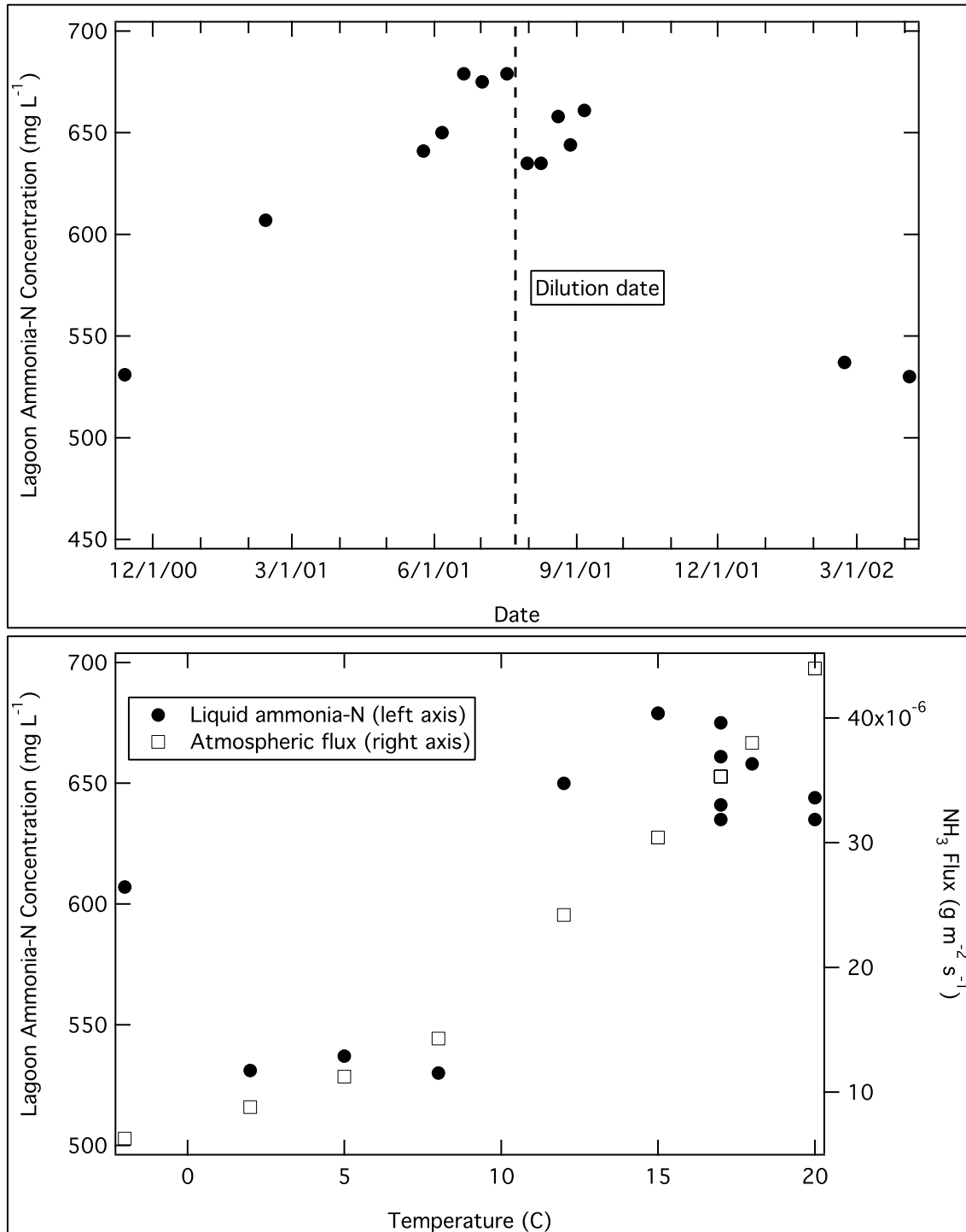


Figure 5.2: Top panel shows lagoon 2 ammonia-N concentrations (mg L^{-1}) as a function of time with the dashed line showing the date waste from lagoons 3 and 4 were added diluting the lagoon concentration. Bottom panel shows lagoon ammonia-N concentration as a function of temperature (circles on left axis) and theoretical flux based upon temperature (squares on right axis).

The equilibrium between NH_3 and NH_4^+ in solution depends upon the pH of the solution and can be described by the equilibrium constant K_d .

$$K_d = [\text{H}_3\text{O}^+(\text{aq})] \frac{[\text{NH}_3(\text{aq})]}{[\text{NH}_4^+(\text{aq})]} \quad (5.7)$$

where [] denotes molar concentrations.

The equation of Kamin et al. (1979) was used to determine the partitioning between NH_3 and NH_4^+ in solution.

$$K_d = 10^{-\left(0.09018 + \frac{2729.92}{\text{Temperature}(K)}\right)} \quad (5.8)$$

The concentration of NH_3 released to the atmosphere is governed by the following equation.



The Henry's law constant K_H can be used to calculate the partitioning of NH_3 in the gas and liquid phases. Ni (1999) noted that many different forms of Henry's Law have been used to study NH_3 emissions from waste. A non-dimensional form of the Henry's Law equation was used

$$K_H = \frac{\text{NH}_3(\text{a,o})}{\text{NH}_3(\text{aq})} \quad (5.10)$$

The equation of Monteny et al. (1996) for NH_3 in water was used for the model.

$$K_H = 1384 + 1.053^{(293 - \text{Temperature}(K))} \quad (5.11)$$

5.4 Results and Discussion

Figure 5.3 shows typical high time resolution concentration data collected downwind of lagoon 2 at approximately 1 second resolution. High NH_3 concentrations correspond to the wind advecting across the lagoon to the DOAS measurement path. When the winds are from the southwest the DOAS minimum detection limit is evident. The NH_3 plume moves on and off the instrument path as the wind changes direction. When the plume blows away from the the instrument path the detection limit of a few ppbv is evident.

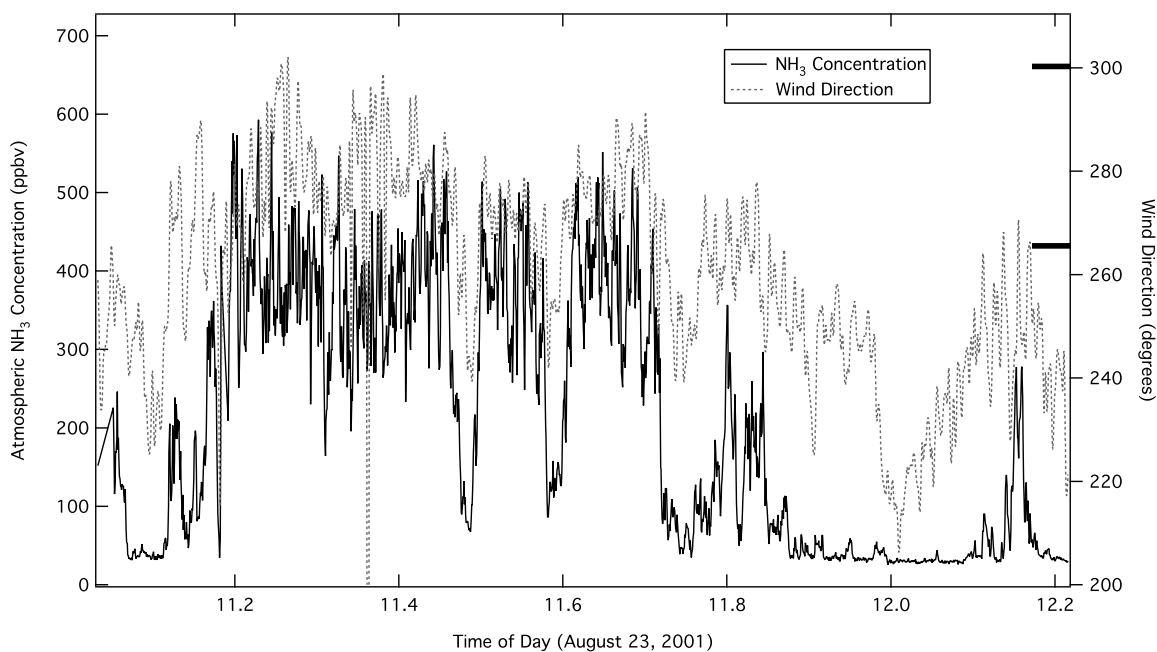


Figure 5.3: Ammonia concentration (solid line, left axis) 50 m downwind of lagoon 2 measured approximately every second and wind direction (dashed line, right axis). Bars on right axis mark optimal wind direction.

5.4.1 Tracer Experiments

Tracer experiments and concentration measurements were only made when there was a steady west wind. All concentration data were averaged to 30 minutes.

The SF_6 line source and concentration tracer ratio data were first analyzed to test the approximation of σ_z using values of a and b based upon stability from Busse and Zimmerman

(1973). The stability approximation of σ_z was found to overestimate the downwind concentration. The error was greatest at lower wind speeds. Plotting σ_z versus wind speed showed the wind speed dependence and average values of σ_z were obtained for each 1 m s^{-1} change in wind speed. Wind speed dependent σ_z values were calculated by linearly interpolating between the values of a and b given by Busse and Zimmerman (1973) and then recalculating σ_z , a and b values that corresponded to the wind speed σ_z values were then used.

The measured NH_3 flux values ranged from $30 \mu\text{g m}^{-2} \text{ s}^{-1}$ at an air temperature of 11° C to $150 \mu\text{g m}^{-2} \text{ s}^{-1}$ at an air temperature of 27° C . Sommer et al., 1993 reported an emission rate of $30 \mu\text{g m}^{-2} \text{ s}^{-1}$ so the results are comparable. The area source flux equation and the calculated dispersion variables were then used to calculate the downwind concentration.

5.4.2 Emission Algorithm

The theoretical model discussed previously was used to develop an emissions model for NH_3 fluxes from dairy lagoons. The model was used with the area source flux equation to calculate downwind concentrations which were then compared to measured concentrations. The convective mass transfer coefficient of h_m was empirically fit to the data; the final value was 5.8×10^{-4} . Ni (1999) reported convective mass transfer values ranging from 1.17×10^{-3} to 1.3×10^{-6} . The modeled concentrations were compared to actual downwind concentrations using the area source emissions equation. The model base case conditions were: ammonia-N concentration: 660 mg L^{-1} except for temperatures below 10° C when it was 530 mg L^{-1} , pH was 7.8, the lagoon temperature measured at a depth of 10 cm, the air temperature was measured at the corner of the lagoon at 3 m.

Figure 5.4 shows the modeled concentration downwind of the lagoon against the measured concentration downwind of the lagoon for 130 half-hour averaged measurements. The top panel shows the model using the lagoon temperature at a depth of 10 cm for the liquid surface temperature and the bottom panel shows the model using the ambient air temperature as the lagoon surface temperature. The model using the air temperature had an error of 21%

while using the lagoon temperature the error was 24%. The difference in model performance is not significant. Using the lagoon temperature did over predicted at lower temperatures while using the air temperatures produced more scatter at higher temperatures. The error at low temperatures using the lagoon temperature could be due to differences in using a Henry's law constant for water versus manure or that the conduction of heat through the slurry to a depth of 10 cm does not reflect the actual surface temperature.

5.4.3 Annual Emissions

The annual lagoon emissions from the dairy were calculated in three ways to test different assumptions used in modeling dairy lagoon emissions. The first way is representative of the actual operating conditions of the dairy, the second assumes that the dairy uses one big lagoon for the entire year equal in size to all of the current lagoons, and the third is one lagoon sized according to literature design criteria. Meteorological data for 2001 measured from the rooftop of a building on the WSU campus 8 km distant was used as input. The emissions from all lagoons were modeled with the theoretical emissions equations using the air temperature as the input. It was assumed that at ambient wind speeds of 1.5 m s^{-1} and below the lagoon surface wind speed was 0 so the emissions were 0 and at temperatures below $-3 \text{ }^{\circ}\text{C}$ the lagoon was frozen.

For lagoon 1, the surface area is 230 m^2 and the concentration was assumed to be that of lagoon 2. Lagoon 2 has a surface area of 5900 m^2 . Lagoons 3 and 4 are identical and each have a surface area of 4800 m^2 . Lagoons 3 and 4 are emptied at the end of August and then they are filled again starting in November. It was assumed that additional waste was added in January, March, and May. Due to the fact that they do not receive waste all the time there is a net loss of N in the lagoons due to NH_3 volatilization. Lagoons 3 and 4 are joined by a pipe but when waste is pumped into them it is pumped into lagoon 3, therefore they are not equally mixed. The differential filling of the lagoons is demonstrated by liquid samples taken July 24, 2001. The ammonia-N concentration in lagoon 3 was 439 mg L^{-1} and lagoon 4 had

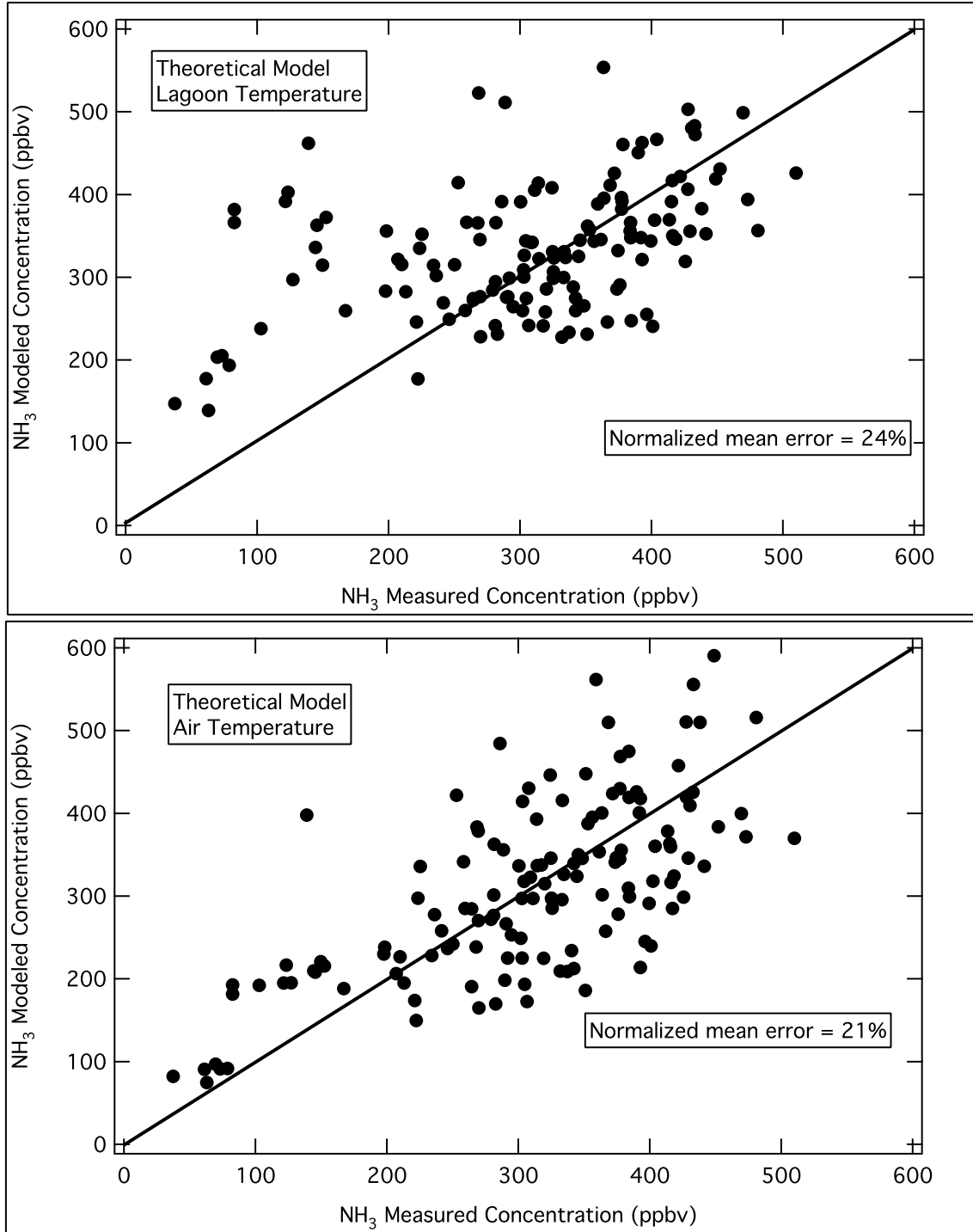


Figure 5.4: Theoretical model of downwind NH₃ concentrations (ppbv). Top panel shows model using lagoon temperature in the model and the bottom panel shows using the air temperature.

a concentration of 226 mg L⁻¹. Because lagoons 3 and 4 only periodically receive additional waste and the concentrations are different an ammonia-N balance approach was used. The concentrations in lagoons 3 and 4 were calculated based upon ammonia-N additions and volatilizations. Initially both lagoons had the same concentration of ammonia-N as lagoon 2 but as NH₃ volatilized the ammonia-N concentration in the lagoon was reduced. When additional waste from lagoon 2 was transferred lagoon 3 received 70% of the mass ammonia-N and lagoon 4 received 30% of the mass ammonia-N. It was assumed that at temperatures above 10° C that the lagoon concentration increased by 20% as was the case for lagoon 2. Under these condition the July modeled concentration for lagoon 3 was 420 mg L⁻¹ and for lagoon 4 it was 210 mg L⁻¹.

The combined annual lagoon 1 and 2 NH₃ emissions were 5200 kg, lagoon 3 released 2900 kg and lagoon 4 emissions were 1600 kg for a total lagoon annual emission of 9700 kg NH₃. The daily emissions for the entire year are shown in Figure 5.5 along with the average daily temperature. The flux is very seasonal and it is also possible to see the emptying of lagoons 3 and 4 at about day 240 and then when they are filled again near day 310. The modeled daily emissions ranged from over 100 kg per day when conditions were warm and windy to 0 when the lagoon was frozen.

The annual emissions were also calculated as if the dairy operated one large lagoon with the combined surface area of all of the lagoons and the ammonia-N concentration of lagoon 2. The annual emissions based upon one large lagoon was 13000 kg. The annual emissions can also be estimated based upon suggested design criteria for lagoons. A simulated lagoon was designed based upon design criteria for anaerobic lagoons (ASAE, 1999). An average design depth of 4 m was chosen and waste volumes were calculated from ASAE (2003). Using the ASAE (1999) design guidelines for lagoons a surface area of 8121 m² was calculated and the annual emissions from one lagoon of that size is 6900 kg.

The most likely estimate of annual emission is 9700 kg (55 kg cow⁻¹ yr⁻¹) based upon the actual operating conditions at the dairy. Assuming all the lagoons at the dairy are full and

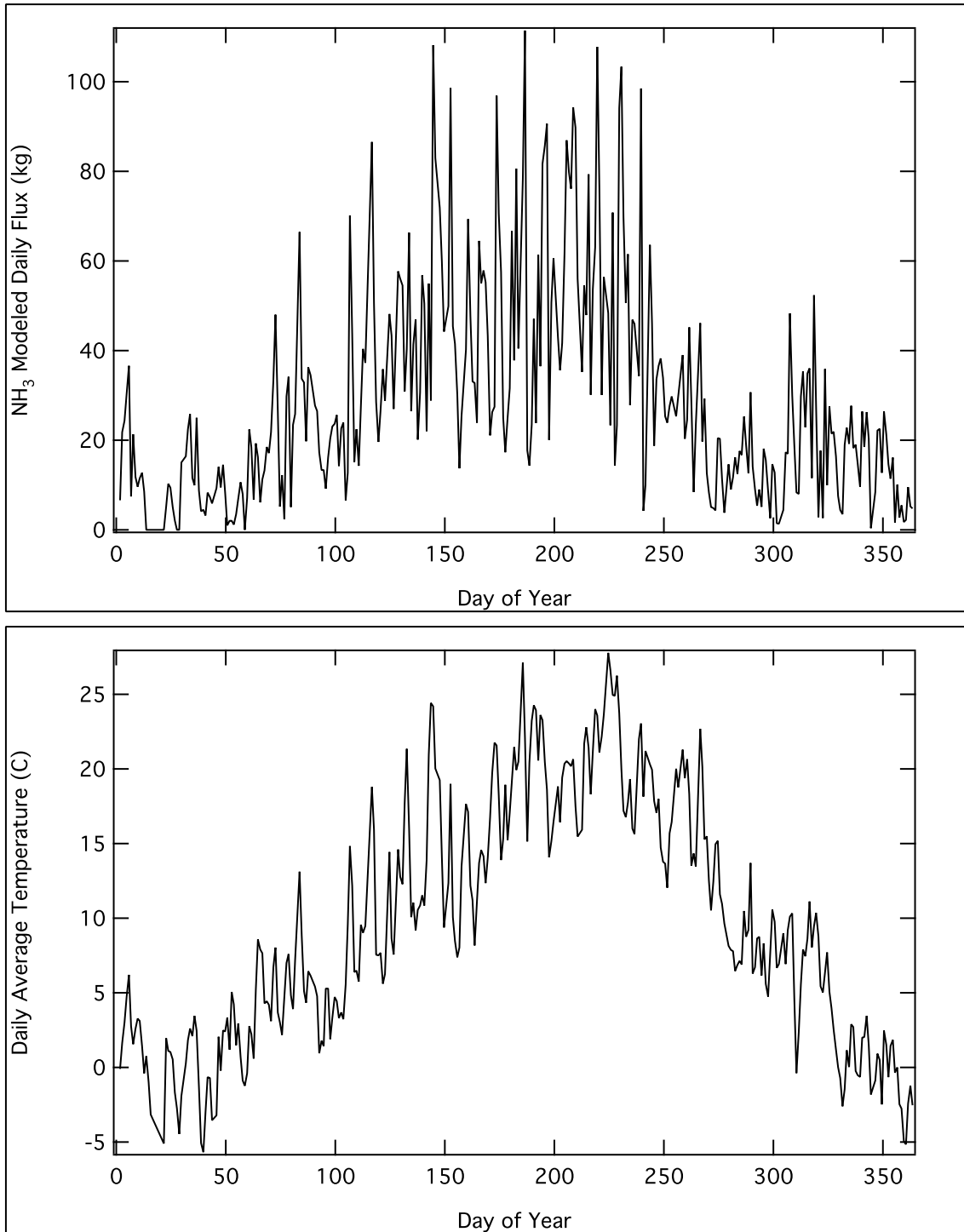


Figure 5.5: Theoretical lagoon model daily NH₃ flux (upper panel) for 2001 and average daily temperature. At day 240 lagoons 3 and 4 were emptied and filled again about day 310.

have the same concentration the annual emissions estimate is 13000 kg or an error of +34%. Using literature design criteria for estimating emissions produced an annual emissions rate of 6900 kg or an error of -29%.

5.4.4 Modeling Sensitivity Analysis

A model sensitivity analysis was performed to understand how model assumptions would impact emissions. The model was evaluated by comparing measured downwind concentrations taken from 2000 to 2003 with modeled concentrations. The measurements were averaged over half-hour time periods and only measurements when the wind was blowing within $\pm 15^\circ$ of straight over the lagoon and the σ_θ was less than 15° were used, 130 measurements were used for the analysis. The area source Gaussian plume equation was used along with the calculated dispersion variables. The statistics to evaluate the models were the mean bias (MB), normalized mean bias (NMB), and the normalized mean error (NME) as given by the following equations.

$$MB = \frac{1}{n} \sum (X_{mod} - X_{meas}) \quad (5.12)$$

$$NMB = \frac{\frac{1}{n} \sum_1^n (X_{mod} - X_{meas})}{\frac{1}{n} \sum_1^n X_{meas}} 100\%. \quad (5.13)$$

$$NME = \frac{\sum_1^n |X_{mod} - X_{meas}|}{\sum_1^n X_{meas}} 100\%. \quad (5.14)$$

where n is the number of data points, X_{mod} is the modeled concentration and X_{meas} is the measured concentration. The model sensitivity analysis is shown in Table 5.1. The base case for the model is using the lagoon temperature, pH of 7.8, and the lagoon ammonia-N concentration of 660 mg L^{-1} . The ammonia-N deviation was added or subtracted from the step function for the biological activity. The deviation of model parameters from the base

case is listed in the first column.

The model performed best using the air temperature instead of the lagoon temperature. This could be due to the depth of the temperature probe (10 cm) not accurately reflecting the surface temperature or a temperature bias in the Henry's law constant for water versus the slurry. Using ambient air temperature does make modeling the NH_3 release easier for air quality models since air temperature is already calculated. Overestimating both the air and lagoon temperature created a larger error in the model than underestimating the temperature. The model was very sensitive to changes in pH. Varying the ammonia-N concentration did not affect the modeled downwind concentration as much as changes in temperature or pH.

5.5 Lagoon Emission Rate Error Analysis

The error in the tracer ratio method can be estimated through a propagation of error analysis. The error in the measurement of the SF_6 emission rate is derived from changes in the flow from the line source due to heating and cooling and errors in measuring the gas flow. Duplicate measurements of the flow from the line source gives an error of $\pm 5\%$ and multiple measurements of the flow shows an agreement to within $\pm 2\%$. The combination of these two uncertainties gives the error from the tracer emission rate of $\pm 7\%$. The error in the measurement of the SF_6 downwind is due to calibration errors and the precision of the measurement. The calibration gases have an accuracy of $\pm 5\%$ and the precision of the measurements is about $\pm 5\%$ for a total error in the SF_6 measurement of $\pm 7\%$.

The uncertainty in the measurement of NH_3 concentration is derived from errors in the NH_3 ultraviolet absorption cross section due to uncertainties in the concentration of the calibration gas. There are also errors in the measurement of the path length, illumination of the spectrograph, shifts and stretches in the spectra due to thermal changes in the spectrograph

Table 5.1: Waste storage model sensitivity analysis for downwind lagoon concentrations from 2000 to 2003. Base case using measured air temperature, pH of 7.8, and ammonia-N concentration of 660 mg L⁻¹ above 10° C and 530 mg L⁻¹ below. Sensitivity statistics: mean bias (MB), normalized mean bias (NMB), and normalized mean error (NME).

Model Base Case Deviation	MB (ppbv)	NMB (%)	NME (%)	Average Flux ($\mu\text{g m}^{-2} \text{s}^{-1}$)
Base Case	0.17	0.055	21	120
Air Temp + 5°C	130	41	43	180
Air Temp + 2°C	46	15	26	140
Air Temp - 2°C	-40	-13	23	110
Air Temp - 5°C	-92	-30	32	88
Lagoon Temp	26	8.5	24	140
Lagoon Temp + 5°C	160	52	53	190
Lagoon Temp + 2°C	75	24	30	160
Lagoon Temp - 2°C	-17	-5.6	25	120
Lagoon Temp - 5°C	-73	-24	34	95
pH = 8.1	340	110	110	260
pH = 7.9	110	0.26	38	170
pH = 7.7	-41	-13	28	110
pH = 7.5	-140	-45	48	69
Ammonia-N + 25%	110	36	38	170
Ammonia-N + 10%	60	19	28	150
Ammonia-N - 10%	-7.3	-2.4	24	120
Ammonia-N - 25%	57	-19	31	100
h_m + 25%	110	36	38	170
h_m + 10%	60	19	28	150
h_m - 10 %	-7.3	-2.4	24	120
h_m - 25%	-57	-19	31	100

and mathematical errors in the retrieval of the concentration. The overall error is estimated to be $\pm 25\%$ (Mount et al., 200).

Lamb et al. (1995) noted that the error in the dispersion coefficient b is due to uncertainties in the power law estimation of vertical dispersion. The use of experimentally derived values reduced the calculated flux by approximately 20%. Thus, the quantifiable error in NH_3 emission flux for the lagoon tracer experiment is $\pm 33\%$. There are a number of systematic unquantifiable errors in the experiment. The tracer flux equation assumes a rectangular area source and uniform emissions. The lagoon is not square and terrain effects of the surrounding area are not known. It was assumed that all areas of the lagoon had equal emissions, but the ammonia-N concentrations were highest closest to the inlet. The experiment also assumed that NH_3 deposition is zero.

5.6 Conclusions

The concentration of NH_3 were measured downwind from a dairy waste lagoon using DOAS and emissions were measured using a tracer ratio method. The NH_3 flux values ranged from 30 to 150 $\mu\text{g m}^{-2} \text{s}^{-1}$ depending upon temperature. The tracer experiments were used to calibrate a Gaussian plume equation and to develop a theoretical emissions model. The theoretical emissions model predicts the downwind concentrations of NH_3 best when using the air temperature as opposed to the lagoon temperature. The normalized mean error of the model using the ambient air temperature as the lagoon temperature input was 21%. The model is very sensitive to changes in pH. The daily lagoon fluxes ranged from over 100 kg per day in the summer to 0 when the lagoon was frozen over. The annual emissions were calculated to be 9700 kg or (55 kg $\text{cow}^{-1} \text{yr}^{-1}$) based upon dairy lagoon operating conditions. If all lagoons were assumed to be full the entire year the total emissions would be 13000 kg and if the lagoons were sized according to literature design criteria the emissions would be 6900 kg.

Chapter 6

Aeration Experiment

Brian Rumburg, Manjit Neger, George H. Mount, David Yonge, Jenny Filipy, Brian Lamb,
Hal Westberg

Department of Civil and Environmental Engineering

John Swain, Ron Kincaid, Kristen Johnson

Department of Animal Sciences
Washington State University
Pullman, Washington 99164-2910

published in
Atmospheric Environment

6.1 Abstract

Ammonia emissions from agriculture are an environmental and human health concern, and there is increasing pressure to reduce emissions. Animal agriculture is the largest global source of ammonia emissions and on a per cow basis dairy operations are the largest emitters. The storage and disposal of the dairy waste is one area where emissions can be reduced, aerobic biological treatment of wastewater being a common and effective way of reducing ammonia emissions. An aeration experiment in a dairy lagoon with two commercial aerators was performed for one month. Liquid concentrations of ammonia, total nitrogen, nitrite and nitrate were monitored before, during and after the experiment and atmospheric ammonia was measured downwind of the lagoon using a short-path differential optical absorption spectroscopy (DOAS) instrument with 1 ppbv sensitivity. No changes in either liquid or atmospheric ammonia concentrations were detected throughout the experiment, and neither dissolved oxygen, nitrite nor nitrate could be detected in the lagoon at any time. The average ammonia concentration at ten sampling sites in the lagoon at a depth of 0.15 m was 650 mg/L and at 0.90 m it was 700 mg/L $\text{NH}_3\text{-N}$. The average atmospheric ammonia concentration 50 m downwind was about 300 ppbv. The 0.90 m depth total nitrogen concentrations and total and volatile solids concentrations decreased during the experiment due to some mixing of the lagoon but the 0.15 m depth concentrations did not decrease indicating that the aerators were not strong enough to mix the sludge off the bottom into the whole water column.

6.2 Introduction

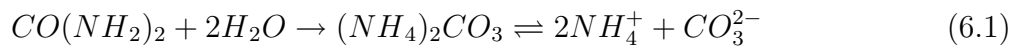
An understanding of ammonia (NH_3) emission rates from U.S. agricultural operations is required to develop effective abatement strategies to minimize the impact on the environment. Agriculture is the largest U.S. source of NH_3 . The National Research Council listed NH_3 from animal feeding operations as the most important atmospheric emission on a global, national and regional spatial scale in a recent report (NRC, 2003). This report also noted

that there is a severe lack of measurement data quantifying NH_3 emissions in the U.S.. Most of the measurement data to date are from Europe where farming practices differ significantly from the U.S. and this, coupled with the complex nature of animal feeding operations, leads to great uncertainty in emissions and inhibits development of effective abatement strategies. Thus, there is a pressing need for good emissions data on NH_3 and tested remediation strategies to limit those emissions.

Atmospheric NH_3 is a major environmental concern because it impacts atmospheric chemistry, sensitive ecosystems and human health. NH_3 is the most abundant basic gas in the atmosphere and its abundance determines precipitation acidity (Warneck, 1988). In the atmosphere NH_3 is removed fairly quickly (1-5 days) by dry deposition because it sticks to most surfaces. Since most ecosystems are reactive nitrogen limited, the deposition of NH_3 can lead to eutrophication of terrestrial and aquatic environments. NH_3 will also react with acidic species such as sulfate (SO_4^-) and nitrate (NO_3^-) to form aerosols of ammonium sulfate and ammonium nitrate. The ammonium aerosols are also removed by deposition but have an atmospheric lifetime 5-10 days and affect a corresponding larger spatial area. For a more complete discussion of environmental impacts and anthropogenic changes to the nitrogen cycle see (Galloway et al., 1995). Ammonium aerosols also affect the radiative transfer of the atmosphere thus impacting global climate change. Since NH_3 is a precursor to ammonium aerosols, which are regulated as part of the U.S. Environmental Protection Agency $\text{PM}_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 microns) National Ambient Air Quality Standards, NH_3 emissions are in effect regulated and control strategies will most likely be implemented in areas out of $\text{PM}_{2.5}$ compliance with high ammonium aerosol levels. High levels of $\text{PM}_{2.5}$ have been shown to affect human health but it is not known if the specific composition of $\text{PM}_{2.5}$ or the mass loading is responsible for the health effects (Schwartz, 1994).

The global atmospheric NH_3 emissions are estimated to be: 45 Tg N yr^{-1} (Dentener and Crutzen, 1994), 43 Tg N yr^{-1} (van Aardenne et al., 2001) and 54 Tg N yr^{-1} (Bouwman et al.,

1997). The overall estimation of the uncertainty in global emissions is about 25% while the local emissions are highly uncertain (Bouwman et al., 1997). NH_3 emissions have increased about five fold between 1890 to 1990 and the increase has been mostly due to increased agriculture. Animal agriculture, specifically animal excreta, is estimated to be half of the global 1990 emissions (van Aardenne et al., 2001). Excreta can form volatile NH_3 in two ways: first, the ammonium carbonate that is formed by the hydrolysis of urea in the urine by the enzyme urease in the feces or the environment can rapidly disassociate according to the following reaction:



The second is the break down of organic nitrogen compounds into amino acids which further degrade to NH_3 and other compounds as shown in the following equation:



In developed countries, and based upon European measurements, Bouwman et al., 1997 estimated the NH_3 -N emissions are 20.4 kg N head⁻¹ year⁻¹ for dairy cows and 7.8 kg N head⁻¹ year⁻¹ for nondairy cattle. Bussink and Oenema, 1998 estimated the range of NH_3 emissions to be between 17 and 46 kg NH_3 dairy cow⁻¹ year⁻¹ due to differences in feed, cow metabolism, waste handling and environmental factors. The overall emissions from farms are very uncertain and this has led to slow implementation of abatement strategies (Bussink and Oenema, 1998). The major losses of NH_3 occur from spreading the waste to fields during disposal, waste storage and cow housing. For remediation strategies to be effective they must limit total emissions, not shift emissions from one source to another.

The storage and land application of waste is one of the largest emission sources from dairies of both NH_3 and odors (Bussink and Oenema, 1998). Many dairies in the U.S. store the manure as either a thick slurry or dilute with water and store in a lagoon. A survey by

the U.S. Department of Agriculture showed over 90% of dairies with 200 or more cows used some type of liquid manure storage system. In the western U.S., 64.5% of dairies use open pit storage lagoons (USDA, 1996). The most cost effective method of lagoon management is anaerobic treatment. Anaerobic treatment requires very little maintenance, no treatment costs, sludge is minimized and nitrogen losses are minimized resulting in the need for less commercial fertilizer for crops. Most lagoons are anaerobic anyway due to the very high concentrations of nutrients. Most of the research into agricultural wastewater lagoons have been conducted on swine lagoons and only a few studies on dairy lagoons. In one of the few studies of dairy lagoons Sweeten and Wolfe, 1994 studied dairy wastewater from three dairies with ammonium concentrations ranging from 116.5 to 356 mg/L and concentrations of NO_3^- 0.3 to 4.7 mg/L indicating they were aerobic lagoons.

Biological removal of nitrogen from wastewater is an inexpensive way of reducing the emission of NH_3 and other offensive compounds. In biological aerobic treatment the proteins and amino acids are broken down to ammonium (NH_4^+) by heterotrophic bacteria and then autotrophic bacteria will further degrade the NH_4^+ into nitrite (NO_2^-) and NO_3^- . This process of nitrification depends upon the the amount of oxygen present and the time required for the degradation to take place. Nitrate is a highly mobile groundwater pollutant causing methaemoglobinaemia in small children. Nitrate removal is possible under anoxic conditions (no dissolved oxygen) where some bacteria are able to utilize as their terminal electron acceptor NO_3^- . The end products of this denitrification is N_2 , carbon dioxide, water and new bacteria cells. Aerobic wastewater treatment is more expensive in terms of power required to deliver enough oxygen to the lagoon for aerobic conditions; it also requires more management to keep the system running properly. Aerobic treatment of piggery waste has been conducted and shown to be fast and effective at reducing odors and nitrogen, after four days of aeration 56% of the total nitrogen was converted to N_2 gas while during shorter time trials almost all nitrogen was conserved (Sneath et al., 1992). Research is attempting to determine the minimum level of oxygen required to treat dairy wastes for NH_3 and odor

reduction (Westerman and Zhang, 1997). It has been suggested that at least 1 to 2 mg/L of oxygen/L of slurry be maintained in the lagoon to ensure enough oxygen for consistent treatment (NZA EI, 1984).

This work is part of an ongoing study, which started in 2000, of the emission of NH_3 and other compounds from the wastewater lagoons, milking cow stalls and sprinkler application of wastewater at a dairy to determine the total emissions and the meteorological factors that influence emissions. An atmospheric tracer technique is being used to measure emissions and to calibrate a Gaussian plume emission model. The results are being implemented into a regional air quality model.

An aeration experiment was conducted with two commercial surface CirCulatorsTM manufactured by Natural Aeration, Inc. which were put into the main storage lagoon of the Washington State University (WSU) Knott Dairy. We studied both the nitrogen compounds in the lagoon and the NH_3 concentrations downwind of the lagoon before, during and after the introduction of the CirCulatorsTM into the lagoon. We measured the lagoon for total nitrogen, $\text{NH}_3\text{-N}$, NO_3^- , NO_2^- and dissolved oxygen in the lagoon as well as the sludge blanket layer build up in the lagoon. Downwind of the lagoon we measured NH_3 using an open-path spectroscopic method that is self-calibrating and avoids the problem of inlet adherence (Mount et al., 2002). This paper discusses the results of an experiment measuring atmospheric and liquid ammonia concentrations before, during and after the introduction of surface aerators into the dairy wastewater lagoon.

6.3 Methods

6.3.1 Knott Dairy Center

The aeration experiment was conducted at the WSU Knott Dairy Center located in Pullman, Washington USA in summer 2001. The dairy has 350 cows of which about 170 are being milked at any one time. Each milking cow weighs approximately 725 kg and produces about

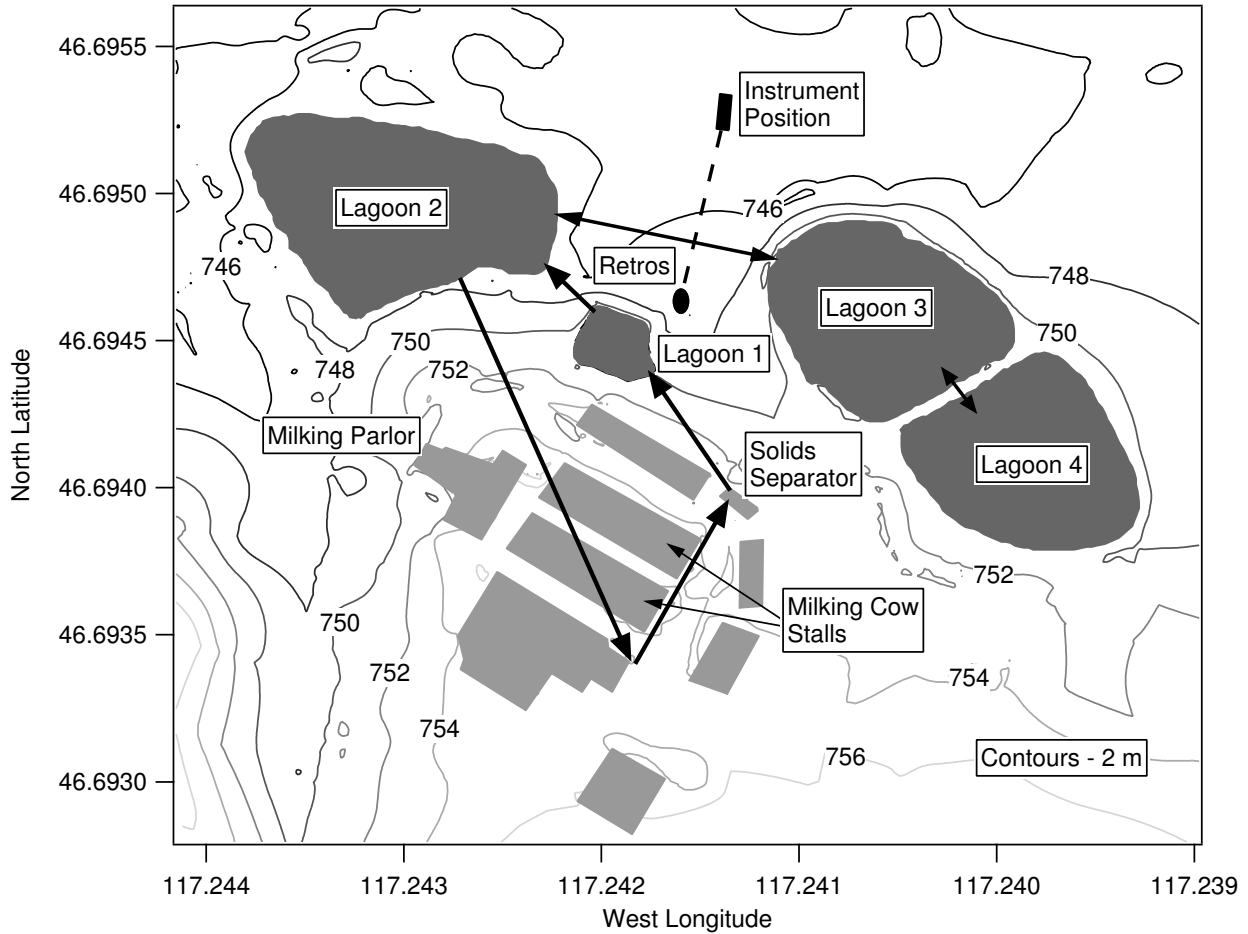


Figure 6.1: Contour map of the Washington State University Knott Dairy. Wastewater lagoons are shown in dark gray and buildings in light gray. Arrows indicate wastewater piping system. Wastewater from lagoon 2 is used to flush the pits at the milking cow stalls when the stalls are scraped. Solids are removed at the solids separator and further removed via gravity settling in lagoon 1. Typical west winds blow across lagoon 2 to the ammonia instrumentation.

40 kg of milk per day. The milking cows are housed in open air stalls with cement floors and are the only contributors to the waste system. A schematic diagram of the dairy is shown in Figure 6.1.

The dairy has four wastewater lagoons which are primarily intended for waste storage until fall application of the wastewater to nearby grass fields using a large sprinkler system. Manure and bedding from the milking cow stall area is scraped into pits daily and flushed

with recycled wastewater from lagoon 2 (surface area 5881 m², average volume 9540 m³) to the solids separator. Fresh water is used for cleaning and approximately 26.5 m³ is added to the wastewater system daily. Approximately 121 m³ of recycled wastewater is used to flush the stall collection pits every day. The solids separator uses a mesh screen to remove solids and solids are composted off site. Liquids continue on to lagoon 1 (surface area 232.3 m², volume 567 m³) where additional solids are removed via gravity settling. Overflow from lagoon 1 then is gravity fed to lagoon 2. Lagoons 3 and 4 (surface area 4766 m², volume 9645 m³ each) are used for long term storage. Wastewater is pumped from lagoon 2 to lagoon 3. Lagoons 3 and 4 are attached with a underwater pipe at the location shown in Figure 1. Wastewater is only pumped into lagoons 3 and 4 periodically when lagoon 2 is full. In the late summer and fall the wastewater is applied to surrounding grass fields using a large sprinkler.

6.3.2 Aerators

Two float-mounted subsurface vertical shaft CirCulatorsTM aerators manufactured by Natural Aeration, Inc. were installed in lagoon 2 at the locations shown in Figure refC4f2. They were positioned to ensure complete mixing of the lagoon. Each CirCulatorsTM has a 1.5 hp electric motor with an reduction gear for an rpm of 120. The impeller has 5 blades and is approximately 62 cm across and is about 62 cm below the water surface when submerged. The company states that the CirCulatorsTM are designed to bring the wastewater up to the surface where oxygen will diffuse into the water, thus introducing oxygen to the system. Specifications state that each will bring 18,900 m³ of water to the surface daily and pull 18,900 m³ of oxygen into the lagoon (Natural Aeration Inc., 2003). For two CirCulatorsTM this is almost four times the average volume of lagoon 2.

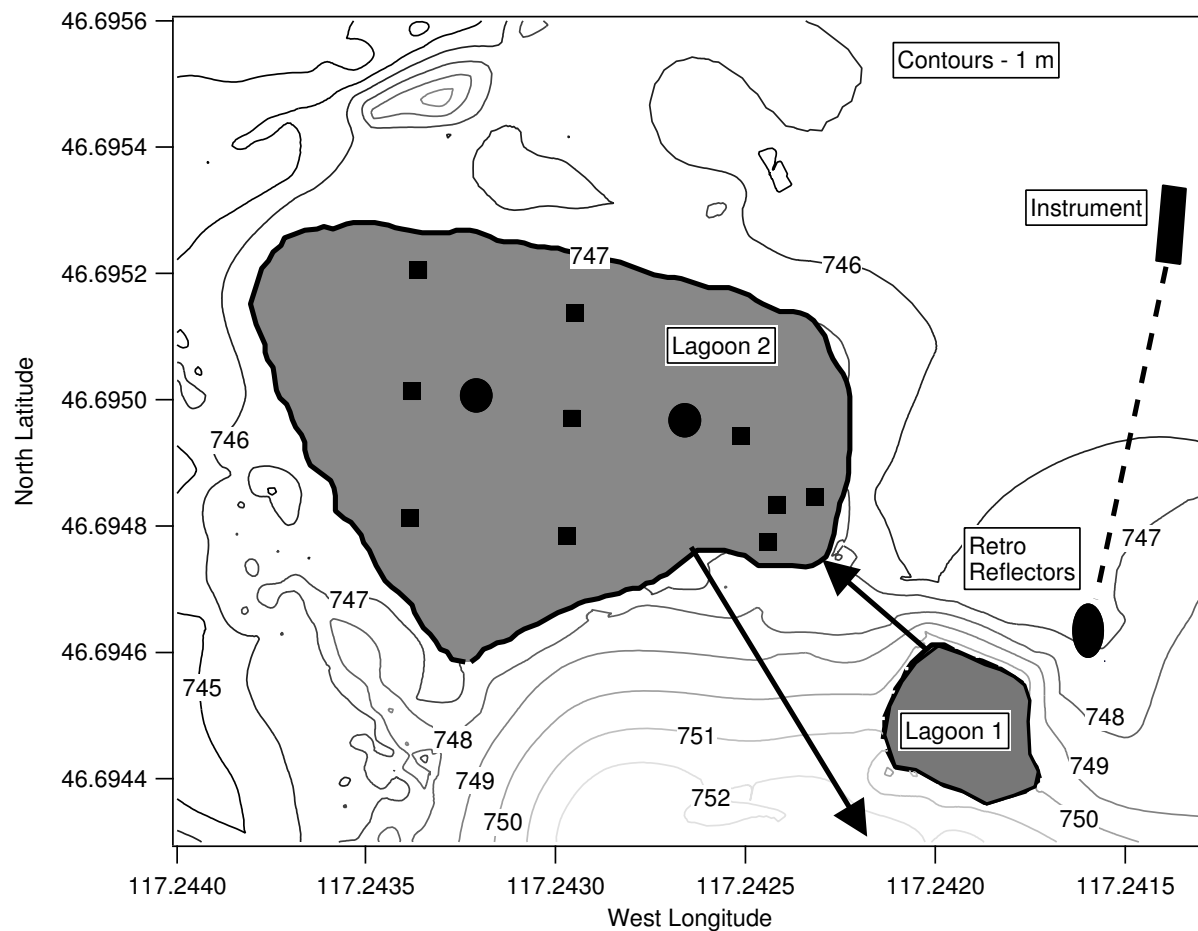


Figure 6.2: Lagoon 2 wastewater sampling sites (boxes) and position of CirCulators™ (circles) and instrument set up downwind with the instrument path denoted by the dashed line.

6.3.3 Water Analysis

The wastewater analysis was part of an ongoing study of the nitrogen balance of lagoon 2. The objective of the water analysis was to measure nitrogen-containing species in the lagoon and to measure the change in sludge levels with the introduction of the CirCulatorsTM. Sampling was carried out approximately every two weeks from May through September 2001. Ten fixed point sampling sites were chosen as shown in Figure 6.2. Samples were collected at depths of 0.15 m and 0.90 m.

After collection the samples were returned to the laboratory where they were immediately analyzed for pH and prepared for analysis of NH_3 , total Kjeldahl nitrogen (TKN), NO_3^- , NO_2^- , total solids and volatile solids. The pH was measured using a Fisher Scientific Accumet Research AR10 pH meter with a poly-body combination electrode with double junction reference. Ammonia-N was analyzed using distillation and titration methods outlined in sections 4500-NH₃ B and 4500-NH₃ E of *Standard Methods for the Examination of Waters and Wastewaters* (APHA,1992). TKN analysis was performed using the macro-Kjeldahl method detailed in section 4500-N_{org} of *Standard Methods*. Nitrate and NO_2^- were analyzed using a Dionex DX-120 chromatograph with a Ionpac AS12-A 4 mm column and a ASRS-Ultra 4 mm suppressor. Total and volatile solids were analyzed using methods outlined in sections 2540 and 2540 E of *Standard Methods*, total solids were dried at 103-105° C and fixed and volatile solids were ignited at 500° C (APHA, 1992).

Sludge depth was measured at eight north-south transects of the lagoon at 5 m intervals. Sludge depth was measured by putting two poles into the lagoon, one with a 30.5 cm square foot, and the other with a 3 cm cap and measuring the difference in the stopping depth of the two poles.

6.3.4 Air Analysis

Atmospheric NH_3 concentrations were measured using an open path differential optical absorption spectroscopy (DOAS) method. The instrument measures the photoabsorption of

NH₃ from 200 to 220 nm. This wavelength region is not illuminated by solar radiation due to the absorption of UV light by ozone in the stratosphere. The instrument consists of a Xenon light source, a collimating telescope to direct the light out along the path, a set of retro reflector mirrors to reflect the light back along the path and a receiving telescope to direct the returning light beam to the spectrograph. The spectrograph is a double crossed Czerny-Turner with a multiplexing silicon array diode detector. The measured absorption spectrum is least squares fit to a calibrated ammonia standard measured in the laboratory and the concentration calculated. The instrument has the advantage that there are no inlet walls for NH₃ to adhere to and also there are no intermediate measurement steps. The sensitivity of the system is a few ppbv and the instrument can make measurements at that sensitivity as fast as every second.

The instrument is housed in a small trailer so that measurements can be made at different locations around the dairy. Further details of the instrument and absorption standard can be found in Mount et al., 2002. Area background measurements were made upwind of the lagoon and the concentrations were below the detection limit of the instrument. The instrument and retro reflectors were positioned approximately 50 m to the west of the lagoon 2 as shown in Figures 6.1 and 6.2 with a path length of 68 m one way.

A Campbell Scientific Weather Station is located at the north east end of the lagoon. Average wind speed and direction at a height of 3 m were measured every five minutes with a R.M. Young 05103 Wind Monitor. A one sigma wind direction deviation was also calculated for each five minute period. Ambient air temperature and relative humidity were measured with a Campbell Scientific Model HMP35C Probe with a Vaisala capacitive humidity sensor at 2 m height.

6.3.5 Experimental

Prior to the introduction of the CirCulatorsTM into lagoon 2, additional wastewater from lagoons 3 and 4 were put into lagoon 2 to raise the level of the lagoon to make the lagoon

deeper and improve the ability of the CirCulatorsTM to circulate the wastewater. The lagoon has a surface area of 5880 m² and prior to the experiment an average depth of 1.61 m for a volume of 9467 m³. After the wastewater addition the depth was 1.89 m, and assuming the same surface area, the new volume was 11113 m³, a volumetric increase of 1646 m³ or 17.4%. The pre-addition NH₃-N concentration in lagoon 2 was 681 mg/L and the TKN concentration was 969 mg/L excluding samples taken with high solids contents due to sampling in the sludge layer. The NH₃-N concentration in lagoon 3 was 439.3 mg/L and lagoon 4 was 226 mg/L. The TKN concentrations were 622.3 and 368.3 mg/L for lagoons 3 and 4 respectively. Most of the wastewater from lagoons 3 and 4 comes from lagoon 3 due to the outlet being in lagoon 3 therefore it was assumed that 70% of the wastewater was from lagoon 3 and 30% from lagoon 4. The dilution should be the result of multiplying the concentrations by the percent of volumes. For NH₃-N the actual concentration was 596 mg/L and the calculated dilution was 627 mg/L which is an error of 5.2% well within the combined 7.6% error for each of the wastewater NH₃-N measurements. For TKN the actual concentration was 855.1 mg/L and the calculated dilution was 895 mg/L which is an error of 4.7%, slightly above the combined 4.2% measurement error. This could be due to insufficient characterization of lagoons 3 and 4 with single pole samples. Due to the assumptions made for the theoretical dilution the actual dilution factor of 1.13 was used and multiplied by all samples subsequent to the start of the aeration experiment.

The CirCulatorsTM were turned on July 30 (day 211) and run continuously until August 28, 2001 (day 239). The experiment was terminated by the start of the wastewater application to the fields. Water analysis was conducted from May 25 to September 6, 2001. Air analysis at location shown in Figure 2 downwind of lagoon 2 was conducted from June 15 until September 4, 2001.

6.4 Results and Discussion

6.4.1 Water Results

The lagoon liquid concentrations of $\text{NH}_3\text{-N}$ and TKN from lagoon 2 are shown in the top panel of Figure 6.3 without the dilution correction for the wastewater addition to lagoon 2 on day 210. The bottom panel of Figure 6.3 shows the same plot of $\text{NH}_3\text{-N}$ and TKN with the dilution correction of 1.13 times all measurements after day 210. The validity of the dilution correction is shown by the fact that the NH_3 concentration did not go down at any other time. The $\text{NH}_3\text{-N}$ concentration does not go down as would be expected if the lagoon was being aerated and the $\text{NH}_3\text{-N}$ being converted to NO_3^- or NO_2^- . In fact the NH_3 concentration slowly rose as the experiment continued as the result of additional waste added to the lagoon. Similar NH_3 concentrations at 0.15 m and 0.90 m during the CirCulatorsTM operation is an indication of successful mixing at least to the 0.90m depth. There was also a reduction in the $\text{NH}_3\text{-N}$ standard deviation of the 0.15 and 0.90 m depth samples indicating good mixing. Similar results were not observed for TKN, however, indicating that a solids concentration gradient remained in the lagoon as shown in Figure 4.

The CirCulatorsTM became less effective at mixing the lagoon as the experiment progressed due to solids islands building up around them. By the end of the experiment the solids build up around the CirCulatorsTM was in some places up to the water surface and surrounded them, limiting their mixing ability. Before the experiment most of the sludge in the lagoon was located within 43 m of the inlet with a sludge depth of between 0.5 to 0.7 m. The sludge blanket in the lagoon was enhanced by the CirCulatorsTM and the sludge depth increased to 0.6 to 1.0 m within 43 m of the inlet. One sampling site had to be abandoned because it could not be reached. The standard deviations of both $\text{NH}_3\text{-N}$ and TKN increased as the experiment continued also indicating the mixing was diminishing.

A dissolved oxygen probe was used in the lagoon near both CirCulatorsTM at the surface and at depth and the reading was below the 0.5 mg/L detection limit of the instrument for the

duration of the experiment. Nitrite and NO_3^- were also analyzed; however all concentrations were below the detection limit of 1.5 mg/L. The pH from each lagoon sample was fairly constant throughout the sampling period and between upper and lower samples and did not change during the experiment. The total average lagoon pH was 7.8 with a high of 7.9 and a low of 7.7.

Since no decrease in $\text{NH}_3\text{-N}$ concentrations could be found and no oxygenated nitrogen compounds could be found, the CirCulatorsTM were not effective in providing enough oxygen to the lagoon to initiate measurable levels of nitrification over the time period of our experiment. Neger, 2002 lists the complete results for each sampling site.

The total and volatile solids in lagoon 2 are shown in Figure 6.4 with the dilution correction. The total solids at the top of the lagoon are quite low and demonstrate the gravitational settling of solids in the lagoon. Volatile solids also decreased more than the effect of dilution. The TKN and solids both displayed the same behavior indicating that the organic nitrogen was associated with the solids, while the NH_3 was not. As discussed above the CirCulatorsTM did not effectively mix the lower portion of the lagoon.

6.4.2 Air Results

Atmospheric NH_3 concentrations downwind of the lagoon are influenced by lagoon concentration, wind speed, wind direction and wind direction deviation over the sampling period. The NH_3 concentrations were combined with meteorological data and sorted for wind directions within 15° of directly over the lagoon towards the instrument path and a wind direction sigma less than 15° . Figure 6.5 shows NH_3 concentration versus wind speed before,

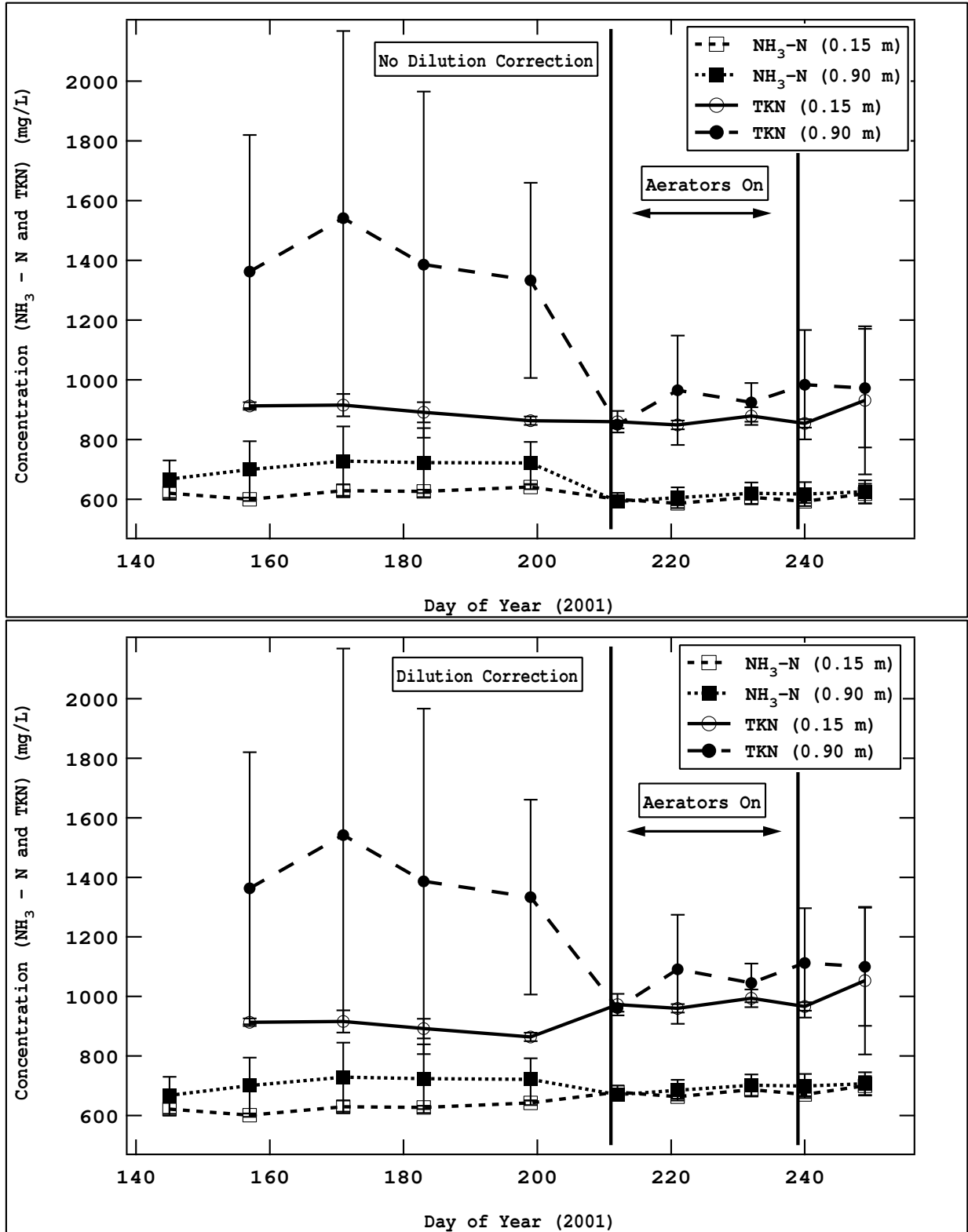


Figure 6.3: Lagoon 2 wastewater average, upper and lower NH₃-N and TKN concentrations without the dilution correction (upper panel) and with dilution correction (lower panel). TKN analysis error averaged 2.1%. NH₃ analysis error averaged 3.8%.

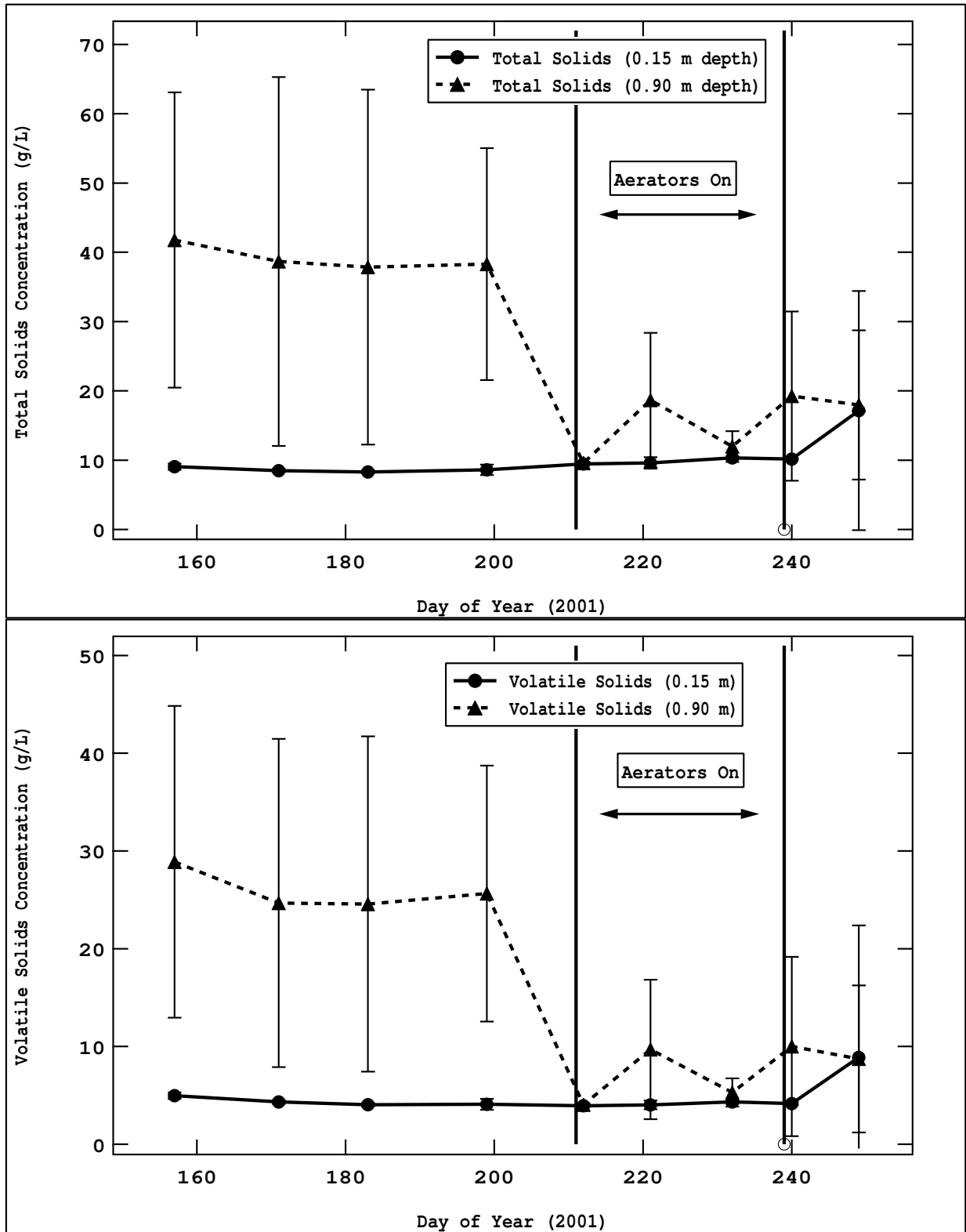


Figure 6.4: Lagoon 2 wastewater total solids (upper panel) and volatile solids (lower panel) using a dilution factor of 1.13 times all samples taken after day 210. Whiskers are one standard deviation from the depth average.

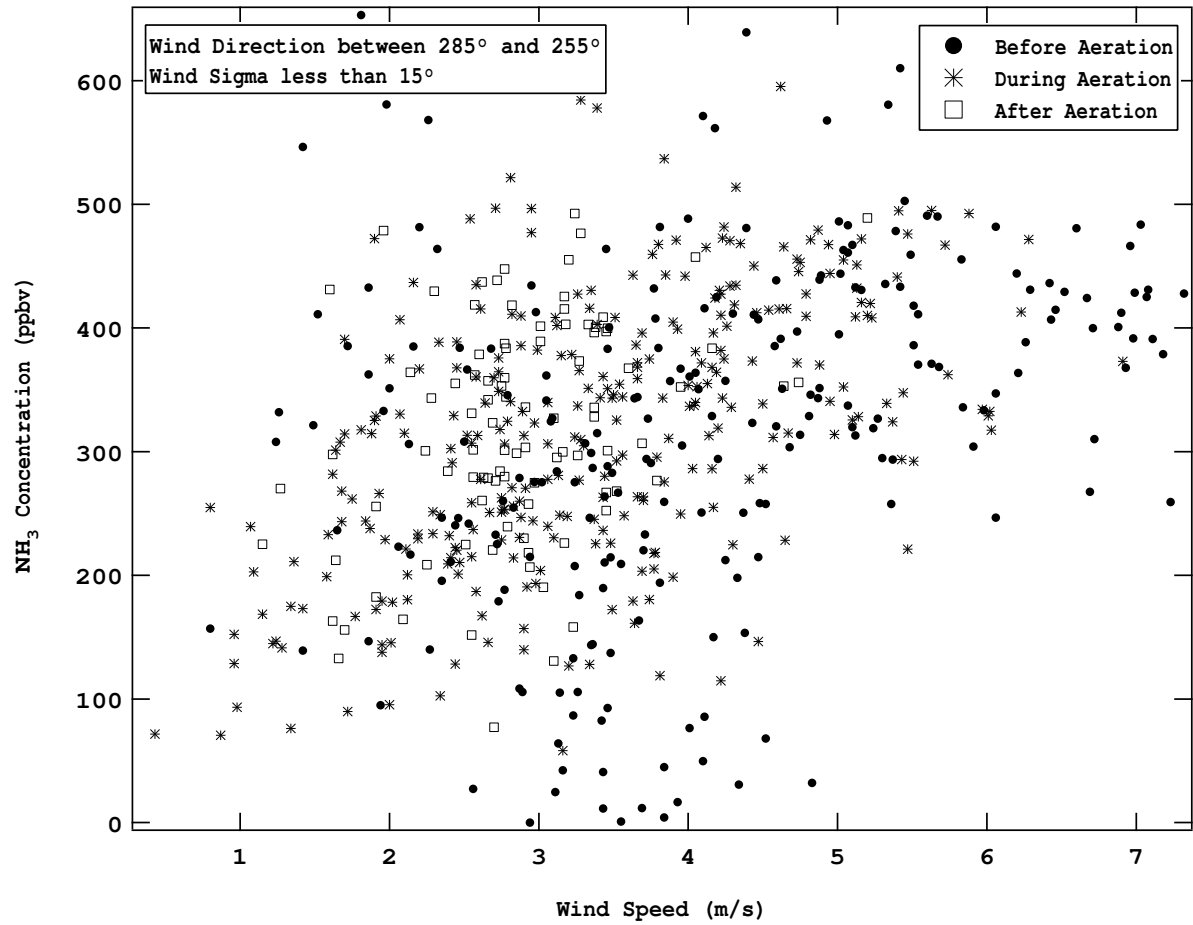


Figure 6.5: Atmospheric NH₃ concentrations downwind of lagoon 2 before, during and after the aeration experiment. Concentrations sorted for wind direction within 15° of directly over lagoon to instrument path and wind direction standard deviation of less than 15°.

during and after the CirCulatorsTM were turned on. There is no decrease in concentrations. At low wind speeds the mass transfer from the lagoon was lower and the dike around the lagoon, which is approximately 1 m above the lagoon surface, might pool the plume. It is also possible that the plume was pooling in the field downwind of the lagoon where the instrument was making measurements. At wind speeds above about 4.5 m s⁻¹ the concentrations were more consistent indicating a more consistent mass transfer and wind field. Figure 6.6 shows NH₃ average and percentile concentrations before, during, and after the aeration experiment. The average air NH₃ concentration was about 300 ppbv downwind. In general, higher wind speeds increased concentrations due to higher mass transfer rates from the liquid to the atmosphere. The effect of temperature on NH₃ concentrations was not as apparent from the data as the effect of the wind speed. The temperature was fairly constant over the experiment at 20°C.

There do not appear to be any discernible trends in the atmospheric NH₃ concentrations. Even the dilution did not affect the concentration downwind which indicates that meteorological factors have a larger influence than a small change in lagoon concentration.

6.5 Conclusions

An experiment was conducted to test the ability of a commercial aerator in a dairy lagoon to reduce liquid NH₃ concentration and the subsequent atmospheric NH₃ emissions. Two commercial aerators were run continuously from July 30 to August 28, 2001. No detectable change in liquid NH₃-N concentration and no detectable levels of dissolved oxygen were found throughout the experiment which indicates that the aerators failed to introduce enough oxygen into the lagoon to biologically degrade the NH₃. TKN and total and volatile solids concentrations at 0.90 m decreased in concentrations due to mixing with the water column but samples at a depth of 0.15 m did not increase indicating that the aerators were not mixing the entire sludge layer from the bottom of the lagoon into the entire water column.

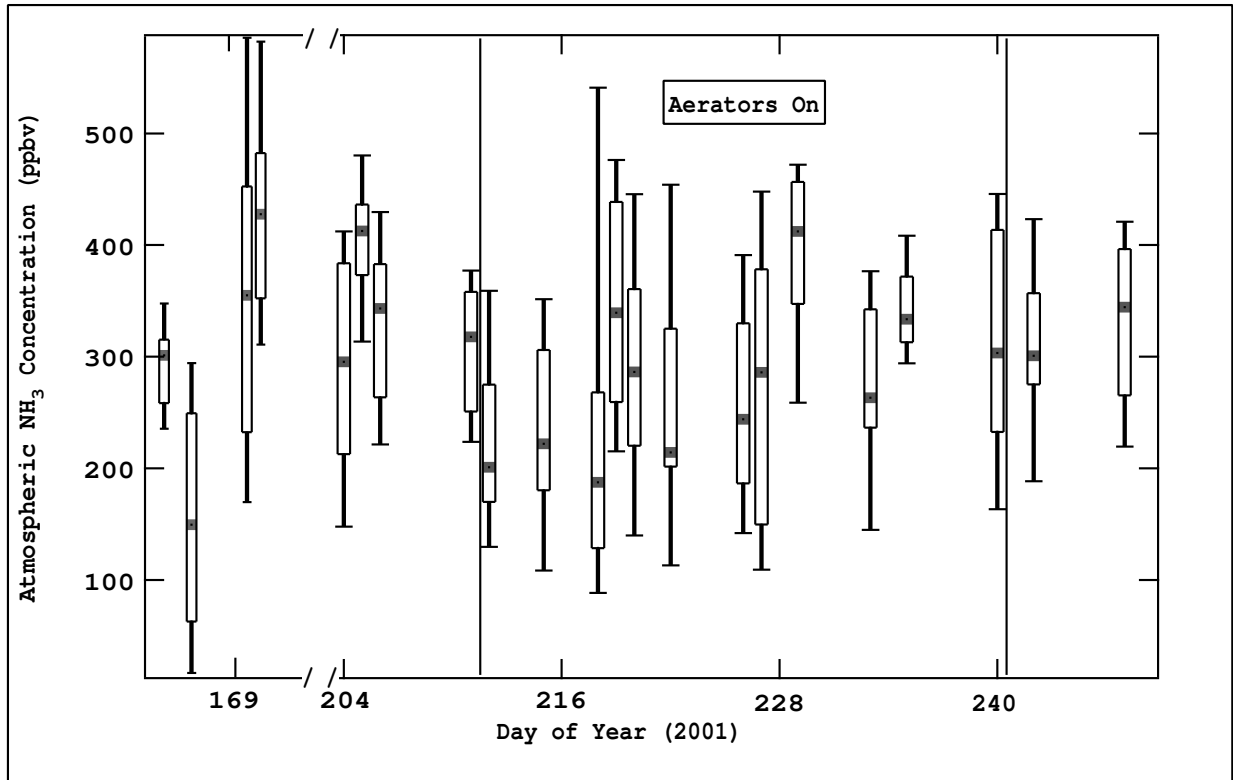


Figure 6.6: Atmospheric NH₃ concentrations downwind of lagoon 2 before, during and after the aeration experiment. Gray marker in box is average NH₃ concentration, box is 25th and 75th percentiles, whiskers are 10th and 90th percentiles. Concentrations sorted for wind direction within 15° of directly over lagoon to instrument path and wind direction standard deviation of less than 15°.

The aerators eventually created large islands of sludge around them limiting their mixing ability. There was no detectible change in atmospheric NH_3 downwind of the lagoon during the experiment confirming the liquid analysis. The average atmospheric NH_3 concentration 50 m downwind of the lagoon was about 300 ppbv throughout the entire experiment.

It is clear from this experiment that for effective abatement of atmospheric NH_3 emissions from dairies there will need to be proven and tested abatement techniques. Due to the lack of current research and the variability of farming practices, further research is needed of dairy lagoon wastes, especially TKN and NH_3 . Extensive research is needed to understand the variability of atmospheric NH_3 emissions from dairies and how to best limit total emissions.

Chapter 7

Slurry Application Emissions

Atmospheric Flux of Ammonia from Sprinkler Application of Dairy Waste

Brian Rumburg, George H. Mount, David Yonge, Brian Lamb, Hal Westberg, Jenny Filipy,

Jay Bays

Department of Civil and Environmental Engineering

Ron Kincaid, Kristen Johnson

Department of Animal Sciences

Washington State University

Pullman, Washington 99164-2910

submitted to

Atmospheric Environment

7.1 Abstract

Ammonia (NH_3) emissions are a growing environmental and human health concern in the U.S.. NH_3 emissions were measured during the sprinkler application of dairy lagoon slurry and field volatilization after application. Of the total ammonical nitrogen entering from the sprinkler pump, 18% volatilized before reaching the ground. Tracer experiments were conducted to determine emissions from the field after application. The initial flux during the tracer experiment was $47 \mu\text{g m}^{-2} \text{s}^{-1}$ and this decreased to $17 \mu\text{g m}^{-2} \text{s}^{-1}$ during the experiment. Ambient measurements showed an exponential decay with time. An empirical exponential equation was fit to the measurement data and it had a mean bias of -0.10 ppbv and a normalized mean bias of -0.050%. A theoretical model had a mean bias of -11 ppbv and a normalized mean bias of -5.5%.

7.2 Introduction

The complex impacts of anthropogenic ammonia (NH_3) emissions on the atmosphere and the environment are not fully understood due to a lack of measurement data and time resolved emission algorithms. This lack of emission rate data in the U.S., along with the factors that influence emissions, makes regulating and mitigating emissions difficult (NRC, 2003). NRC, 2003 listed NH_3 as the most important atmospheric gas emitted from animal feeding operations (AFOs) in the U.S. due to impacts on deposition and haze. In the atmosphere, NH_3 primarily reacts to form ammonium sulfate and ammonium nitrate aerosols which are major constituents of $\text{PM}_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 microns). $\text{PM}_{2.5}$ is regulated as part of the U.S. Environmental Protection Agency National Ambient Air Quality Standards. The main removal mechanism for gaseous NH_3 and aerosol ammonium is wet and dry deposition which can lead to eutrophication of both terrestrial and aquatic ecosystems.

Pre-industrial global NH_3 emissions are estimated to have been $9 \text{ Tg } \text{NH}_3\text{-N yr}^{-1}$ (vanAar-

denne et al., 2001) while current global atmospheric emissions of $\text{NH}_3\text{-N}$ are estimated to be between 45 and 54 Tg N yr^{-1} (Dentener and Crutzen, 1994; vanAardenne et al., 2001; Bouwman et al., 1997). Agriculture accounts for about 79% of the global emissions and almost half of agricultural emissions are from animals (vanAardenne et al., 2001). Ammonia from domesticated animals is produced by the reaction of urea in the urine with urease in the soil or in manure and the biological anaerobic breakdown of organic nitrogen in the waste. Field waste application is a major source of NH_3 emissions from AFOs. Waste can be applied to fields in many different ways, it can be injected into the soil or it can be applied to the surface using various types of sprinklers or tanker trucks. The factors that influence waste emissions are application method, slurry NH_3 concentration, slurry physical and chemical composition, soil physical and chemical attributes, crop uptake rates, pasture canopy height and meteorology.

Sharpe and Harper, 1997 found that during sprinkler application of swine effluent, 13% of the $\text{NH}_3\text{-N}$ volatilized during application and an additional 69% volatilized from the ground during the first 24 hours. Broadcast spreading and band spreading showed similar total emissions from swine slurry (Ferm et al., 1999). Trail hose application was shown to reduce emissions versus splash plates (Sommer et al., 1997). Injecting dairy waste reduced total NH_3 emissions to about 10% of applied $\text{NH}_4^+\text{-N}$ concentrations compared to a splash plate of about 30% for both arable land and grassland (Wulf et al., 2002a). Malgeryd, 1998 found that incorporating the slurry into the soil reduces emissions significantly due to dilution of NH_4^+ in the soil and pH buffering. (Wulf et al., 2002b) found that injection reduced NH_3 emissions but nitrous oxide emissions were greatly increased versus other application methods. The lower dry matter content of swine slurry has been shown to have a lower NH_3 volatilization rate than cattle slurry (Pain et al., 1990). The emissions of NH_3 were shown to be linearly related to dry matter content for the first 6 hours after application and to be nonlinear after that (Sommer and Olesen, 1991). A taller canopy height also reduced emissions and crop growth stage played a role in wheat leaf absorption of NH_3 and thus emissions (Sommer et

al., 1997).

Emission rates from swine slurry of 3.0 and 1.7 $\mu\text{g m}^{-2} \text{s}^{-1}$ for day 2 and 3 after application has been reported by (Galle et al., 2000). Thompson and Meisinger, 2004 measured emission rates from dairy waste application and found that the emission rate during the first 6 hours after application was 56 $\mu\text{g m}^{-2} \text{s}^{-1}$ and 6.1 $\mu\text{g m}^{-2} \text{s}^{-1}$ after that. The spring emission rates were higher, 92 $\mu\text{g m}^{-2} \text{s}^{-1}$ during the first 6 hours and 13 $\mu\text{g m}^{-2}$ after that. Yang et al., 2003 measured the flux of NH_3 from cattle slurry applied at a rate of 109 kg N ha⁻¹ with a NH_4^+ -N concentration of 1830 mg L⁻¹ (assuming a slurry density of 1 kg L⁻¹) and reported a flux for the first, second and third day of 110, 40 and 20 $\mu\text{g N m}^{-2} \text{s}^{-1}$ respectively. Injecting dairy slurry co-fermented with household waste had an emission rate of about 14 $\mu\text{g NH}_3\text{-N m}^{-2} \text{s}^{-1}$ while using a splash plate produced emissions of 97 $\mu\text{g m}^{-2} \text{s}^{-1}$ (Wulf et al., 2002a).

A livestock farm model showed that slurry emissions were influenced by amount of total ammoniacal N on the surface, partitioning between NH_3 and NH_4^+ , surface resistance, soil infiltration rate, evaporation rate and precipitation (Hutchings et al., 1996). Several European slurry experiments were analyzed and modeled with a Michaelis-Menton type model and showed good agreement with measured emissions (Søgaard et al., 2002). An empirical model for emissions from trail hose application beneath a crop canopy was developed; the model explained less than 50% of the emissions during the first 24 hours after application and only 27% of the emissions during seven days of testing of swine and cattle slurry (Sommer and Olesen, 2000). Using a mechanistic model of slurry applied to bare soil showed that soil pH had a large influence on emissions; compared to measurements the model under-predicted emissions during the first day and overestimated thereafter (Génermonet and Cellier, 1997). Wu et al., 2003 developed a model for swine slurry application and found that the model was most sensitive to temperature, soil type, and slurry pH; the model performed well on half of the experimental data analyzed and over-predicted the other half. The infiltration of NH_4^+ was found to be spatially variable and unrelated to slurry, soil or climatic variable (Sommer et al., 2004). The NH_4^+ can bind to the soil which is related to the amount of clay

in the soil and is temperature dependent (Nommik and Vahtras, 1982).

This work is part of a study of the emissions of NH_3 from the milking cows at the Washington State University (WSU) dairy. The objective of this research was to measure the NH_3 emissions during and after the application of dairy cow slurry to a grass field applied with a sprinkler. The emissions from the sprinkler application itself and the subsequent volatilization from the grass field were measured, as well as soil N before and after the application. A tracer experiment was used to determine initial fluxes and a Gaussian plume model was used to determine fluxes after the tracer experiment. A simple empirical model was fit to the data and a theoretical model was built to understand the physical factors that influence the emissions.

7.3 Experimental

Figure 7.1 shows the sprinkler applying waste to the grass field. The normal depth of slurry application to the fields is approximately 5 cm. This is achieved by setting the sprinkler to spray in a semi-circular pattern for 2 hours and then it is moved for an additional 8 hours at a rate of 30 m hr^{-1} . Due to the emissions from both the sprinkler and from the field under normal operating conditions, it was impossible to measure the emissions during actual application. To differentiate the emissions from the sprinkler application and volatilization from the field, an experiment was conducted where the sprinkler was left in one location for four hours and then turned off. Sprinkler emissions were measured by taking samples from the sprinkler pump at the lagoon and bottles were placed around the applied area along north-south and east-west transects. The bottles were placed at distances of 10, 22, 35 and 48 m from the sprinkler. The difference in concentrations between the pump inlet and field bottles gives the volatilization from the sprinkler. To quantify emissions from the field after application, atmospheric tracer experiments were conducted after the sprinkler was turned off to determine the flux from the slurry applied to the field and to calibrate a Gaussian plume model of emissions when the tracer experiments were not being conducted.



Figure 7.1: Sprinkler applying waste to the grass field.

In addition, soil samples were taken before and after the application to understand how the N was moving through the soil.

7.3.1 Dairy Information

The WSU dairy is located approximately 8 km south of Pullman, Washington USA (N 46° 43.8', W 117° 10.1'). It has approximately 175 Holstein milking cows that contribute waste to the lagoon system. The milking cows are fed a diet of 26 kg of feed per day on a dry matter basis, the crude protein is approximately 19%. Milk production is averages 41 kg per day per cow. The cows are housed in a three-sided freestall barn with a concrete floor that is scraped daily. The waste is scraped into pits that are flushed with recycled wastewater from the slurry lagoon. The waste then goes to a solids separator where solids greater than 0.3

cm are removed. Additional solids are removed via a high solids settling lagoon. Waste from the high solids lagoon goes to a low solids lagoon and the dairy has two long term storage lagoons. A more complete description of the lagoons and the N content can be found at Neger, 2002 and Rumburg et al., 2004.

The lagoons are pumped out annually in the late summer and early fall. The WSU dairy uses a "Big Gun" sprinkler (Nelson Irrigation, Walla Walla, Washington) on a traveling reel. The sprinkler has a coverage radius of 50 m depending upon wind conditions. The pump has a discharge of $95 \text{ m}^3 \text{ hr}^{-1}$. The sprinkler reel has 280 m of hose and the area applied during application is approximately 32000 m^2 .

Waste was applied to an unirrigated grass field that had been grazed by cattle. At the time of the experiment, the grass was past the wilting point and the grass canopy was approximately 10 cm in height and partially upright in places and partially laying down due to the grazing by the cattle.

7.3.2 Liquid Analysis

After collection, bottle samples were returned to the laboratory where they were immediately analyzed for pH and prepared for analysis of NH_3 and total Kjeldahl nitrogen (TKN). Ammonia-N was analyzed using distillation and titration methods outlined in sections 4500- NH_3 B and 4500- NH_3 E of *Standard Methods for the Examination of Waters and Wastewaters* (APHA, 1992). TKN analysis was performed using the macro-Kjeldahl method detailed in section 4500- N_{org} of *Standard Methods*.

7.3.3 Soil Analysis

Soil samples were taken to analyze ammonia-N as well as NO_3^- before the sprinkler was turned on and then one day after the sprinkler was turned off. Soil samples coincided spatially with the liquid sample bottles. Four background samples were taken before the experiment. Samples were collected at two depths: 0 to 7.5 cm and 15 cm to 23 cm. After

the slurry application, soil samples were obtained at depths of 0 to 1 cm, 4 to 8 cm, 8 to 15 cm and 15 to 23 cm. The ammonia and ammonium samples were extracted using 2M KCl and analyzed by a reaction with alkaline phenol and hypochlorite to form indophenol blue in an amount that is proportional to the ammonia concentration. The blue color is intensified with sodium nitroferricyanide. The absorbance is measured at 660 nm (EPA, 1994). The nitrate concentration is determined by reacting the nitrate with cadmium-copper to reduce nitrate to nitrite. Nitrite concentration is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride and detecting colorimetrically.

7.3.4 Air Analysis

Atmospheric NH_3 was measured using an open path differential optical absorption spectroscopy (DOAS) method as described in Mount et al., 2002. The instrument measures the photoabsorption of NH_3 in the mid-ultraviolet from 200 to 235 nm. The spectrograph is housed in a trailer along with the Xenon light source, collimating and collecting optics. Retro reflectors were used to direct the light beam to the collecting optics. The spectrograph is a double crossed Czerny-Turner with a silicon array diode detector. Since the instrument does not have any collection inlets it is free of measurement artifacts due to NH_3 adsorbing and desorbing from inlet walls. The instrument has a very high signal to noise ratio and thus the instrument can measure with high precision as fast as every second. The detection limit is a few ppbv. For this experiment one second spectra were co-added and recorded approximately every five minutes. The instrument was set up 75 m downwind of the sprinkler and the total measurement path length was 200 m.

7.3.5 Sulfur Hexafluoride Tracer Technique

An area source tracer technique first discussed by Ludwig et al., 1993 was used to calculate the flux from the slurry applied to the field. In this approach, a tracer is released as close as possible upwind of the area source, at a known rate and is measured downwind at the

same location as the concentration from the area source. Knowing the tracer release rate and downwind concentration it is possible to calculate the atmospheric dispersion. The atmospheric dispersion then can be used to calculate the emissions from the area source as shown below. The best conditions for tracer experiments are a steady wind so turbulence is the dominant dispersion mechanism and small σ_θ so the tracer plume goes over the area source. For this experiment the tracer source was a line source and the line source was placed at the upwind edge of the slurry in the field. The method has been used to measure emissions of natural gas from urban areas (Lamb et al., 1995; Shorter et al., 1997), hydrocarbons from refinery waste impoundments (Howard et al., 1992), and greenhouse gases from cattle processing waste lagoons (Eklund, 1999). Tracer techniques have been shown to be in good agreement with other flux measurement techniques (Lamb et al., 1996). The equation for the concentration downwind of an infinite line source is the following

$$C_l = \frac{2Q_l}{ax^b u \sqrt{2\pi}} \quad (7.1)$$

where C_l is the line source concentration at ground level (g m^{-3}), Q_l is line source emission rate ($\text{g m}^{-1} \text{s}^{-1}$), a and b are an approximation of the vertical standard deviation based upon a distance x (m) and wind speed u (m s^{-1}). The vertical standard deviation is denoted by x and the suggested values of the coefficients a and b are given by (Busse and Zimmerman, 1973).

For an area source the above equation can be integrated to yield:

$$C_A = \frac{2Q_A(X_u^{1-b} - X_d^{1-b})}{ua(1-b)\sqrt{2\pi}} \quad \text{for } b \neq 1 \quad (7.2)$$

C_A is the area source concentration at ground level (g m^{-3}), Q_A is the area source emission rate ($\text{g m}^{-1} \text{s}^{-1}$), X_u is the distance to upwind edge of area source (m) and X_d is the distance to downwind edge of area source (m).

The area source and line source equations can be combined and solved for the flux from

the area source. The only unmeasured variable is b .

$$Q_A = \frac{C_A Q_l (1 - b)}{C_l (X_u^{1-b} - X_d^{1-b}) x^b} \quad (7.3)$$

The SF₆ line source was placed at the upwind edge of the applied slurry. Downwind samples were collected at a rate of 1 mL per minute over 30 minute periods. The syringes were then immediately taken to the laboratory and analyzed using a HP 5880A gas chromatograph (Hewlett Packard, Palo Alto, CA) and standards from Scott Specialty Gases (Plumsteadville, PA). Line source emission rates were measured using a Alltech Digital Flow Check (Alltech, Deerfield, IL) flow meter. The line source was set up along the upwind edge of the applied area and the syringe samplers were placed along the instrument path approximately 10 m from the down wind edge of the applied area. The open path DOAS measurements were average to coincided with the syringe samples.

7.4 Emissions Modeling

7.4.1 Empirical Model

Due to the complexities of emissions and the many factors that must be known to accurately model emissions, a simple empirical model was fit to the field emissions flux data. A simple empirical model also has the benefit that it is computationally easy for air quality models to evaluate. The data requirements are also greatly reduced.

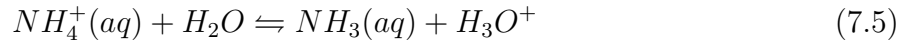
7.4.2 Theoretical Model

A mechanistic model was also tested to determine the relationship between the physical factors influencing the emissions of NH₃. The basis of the model is the convective transfer of NH₃ from the solution to the free atmosphere. The convective mass transfer model between the air-water interface is given by the following equation

$$q_a = h_m(C_{a,0} - C_{a,\infty}) \quad (7.4)$$

Where q_a is the flux per unit area, h_m is the convective mass transfer coefficient and $C_{a,0}$ is the concentration at the interface and $C_{a,\infty}$ is the concentration in the free air stream. Ni, 1999 has a complete discussion and review of mechanistic models related to the release NH_3 from animal wastes.

The NH_3 is in equilibrium with NH_4^+ depending upon the pH of the solution according to the following relationship



The molar equilibrium between NH_3 and NH_4^+ in solution depends upon the pH of the solution and can be described by the equilibrium constant K_d .

$$K_d = [\text{H}_3\text{O}^+(aq)] \frac{[\text{NH}_3(aq)]}{[\text{NH}_4^+(aq)]} \quad (7.6)$$

Kamin et al., 1979 developed the following equation to describe the equilibrium constant between NH_3 and NH_4^+ in solution.

$$K_d = 10^{-\left(0.09018 + \frac{2729.92}{\text{Temperature}(K)}\right)} \quad (7.7)$$

The concentration of NH_3 released to the atmosphere is governed by the following equation.



The Henry's law constant K_H can be used to calculate the partitioning of NH_3 in the gas and liquid phases. The equation of Monteny et al., 1996 for NH_3 in water was used to represent K_H the model.

$$K_H = 1384 + 1.053^{(293 - \text{Temperature}(K))} \quad (7.9)$$

In addition to the reactions in solution, the NH_4^+ will bind to the soil matrix. The adsorption isotherm of swine waste given by Fernando et al., 2005 was chosen due to the N concentrations being similar and the soils both being silty loams. The equilibrium between the NH_4^+ in solution and bound to the soil matrix was described using the following Langmuir isotherm equation

$$q_e = \frac{b_e K C_e}{1 + K C_e} \quad (7.10)$$

where q_e and C_e are the equilibrium concentrations in the solid (mg kg^{-1}) and liquid phases in (mg L^{-1}) and the variable b_e is in $\text{mg NH}_4^+\text{-N kg}^{-1}$ soil and K is 5.6×10^{-3} .

7.4.3 Water content at the soil surface

The HYDRUS-1D model by Simunek et al., 2005 was used to calculate the water content of the soil at the surface. It models the infiltration of water through the soil by solving the Richards' equations for unsaturated and saturated water flow. The heat, solute transport and root uptake modules were not used. The soil is a Thatuna silt loam with an approximate bulk density of 1.35 Mg m^{-3} . The default soil parameters for a silt loam were used except for the following given by Fuentes et al., 2004: residual water content of the soil was set at 0.001, the saturated water content was set at 0.53, the α parameter in the soil retention function was 0.234 and the n parameter in the soil retention function was set at 1.147.

7.4.4 Soil surface temperature

The slurry temperature at the soil surface was assumed to be the same as the soil surface temperature and was calculated using an energy budget approach. The soil temperature was modeled based upon the energy balance at the soil surface. The radiation incident upon the soil surface was calculated based upon the methods described by Campbell and

Norman, 1998 and Généronnet and Cellier, 1997. The grass canopy was modeled using a leaf area index of 1. The model iteratively solved for the soil temperature and then solved for the NH_4^+ in the liquid and solid phases. The NH_3 at the surface was then calculated and a convective mass transfer coefficient was calculated to bring the model into agreement with the observations.

7.5 Results and Discussion

7.5.1 Slurry Sprinkler Volatilization

Four samples were collected from a pump spigot at the lagoon while the pump was running. The average TKN concentration was 1020 mg L^{-1} with a standard deviation of 43 and the average ammonia-N concentration was 717 mg L^{-1} with a standard deviation of 26. The ammonia-N and TKN concentrations and depth of slurry collected from the field bottles are shown in Table 7.1. Two of the bottles were flooded when the sprinkler turned off, other bottles did not capture measurable amounts of slurry due to strong winds. The depth data indicate that the expected application depth of 5 cm was not achieved at any location. The average ammonia-N concentration of the bottles is 589 mg L^{-1} giving a volatilization rate of 18% of the ammonia-N in solution. This assumes that all of the waste coming out of the sprinkler impacts the ground, this is most likely not the case so the volatilization rate is probably conservative. The slurry could be felt 100 m from the sprinkler during strong wind gusts.

7.5.2 Soil N Results

Figure 7.2 shows the soil ammonia-N and TKN data. The slurry infiltrated into the top 8 cm of the soil during the first 24 hours as shown by the increase over background in the increased values of ammonia-N over background. In some cases the ammonia-N concentra-

Table 7.1: Slurry experiment field bottle concentrations of ammonia-N and TKN along with depth of slurry in the bottle. Location is direction relative to sprinkler and distance from sprinkler in m. Only bottles with measurable amounts of slurry are shown, *a* denotes bottles flooded when the sprinkler turned off.

Location	Ammonia-N (mg L ⁻¹)	TKN (mg L ⁻¹)	Depth (cm)
N - 10	a	a	a
E - 10	618	841	3.2
S - 10	a	a	a
W - 10	573	841	1.9
N - 22	581	846	3.8
E - 22	592	838	2.5
S - 22	622	905	1.3
W - 22	546	835	1.6
E - 35	605	842	3.2
E - 48	573	837	1.6

tions increased even at depths of 15 cm most likely due to pooling in low spots. The NO₃⁻-N concentrations also increased over background indicating aerobic bacteria in the soil, which is most likely due to variations in the field as it would take more than 24 hours for the aerobic bacteria to metabolize the TAN from the anaerobic slurry. The sites with high ammonia-N did not necessarily have high NO₃⁻-N concentrations.

The average concentration in the top 1 cm of the soil was 126 ammonia-N mg kg⁻¹ soil after 24 hours. The average concentration at the 1 to 8 cm depth was 78.5 ammonia-N mg kg⁻¹. The average concentration at the 9 to 23 cm depth was 20.2 ammonia-N mg kg⁻¹ which is background concentrations. The maximum infiltration of the slurry was 8 cm in 24 hours. The amount of slurry applied varied from 3.8 cm to 1.3 cm. The locations with the higher application rates did not correspond with the highest soil concentrations.

7.5.3 Air Results

The concentration of NH₃ during the experiment is shown in Figure 7.3 along with wind speed and direction. The highest concentrations correspond to when the sprinkler was operating. The concentration data also show much higher concentrations during the daytime. At night,

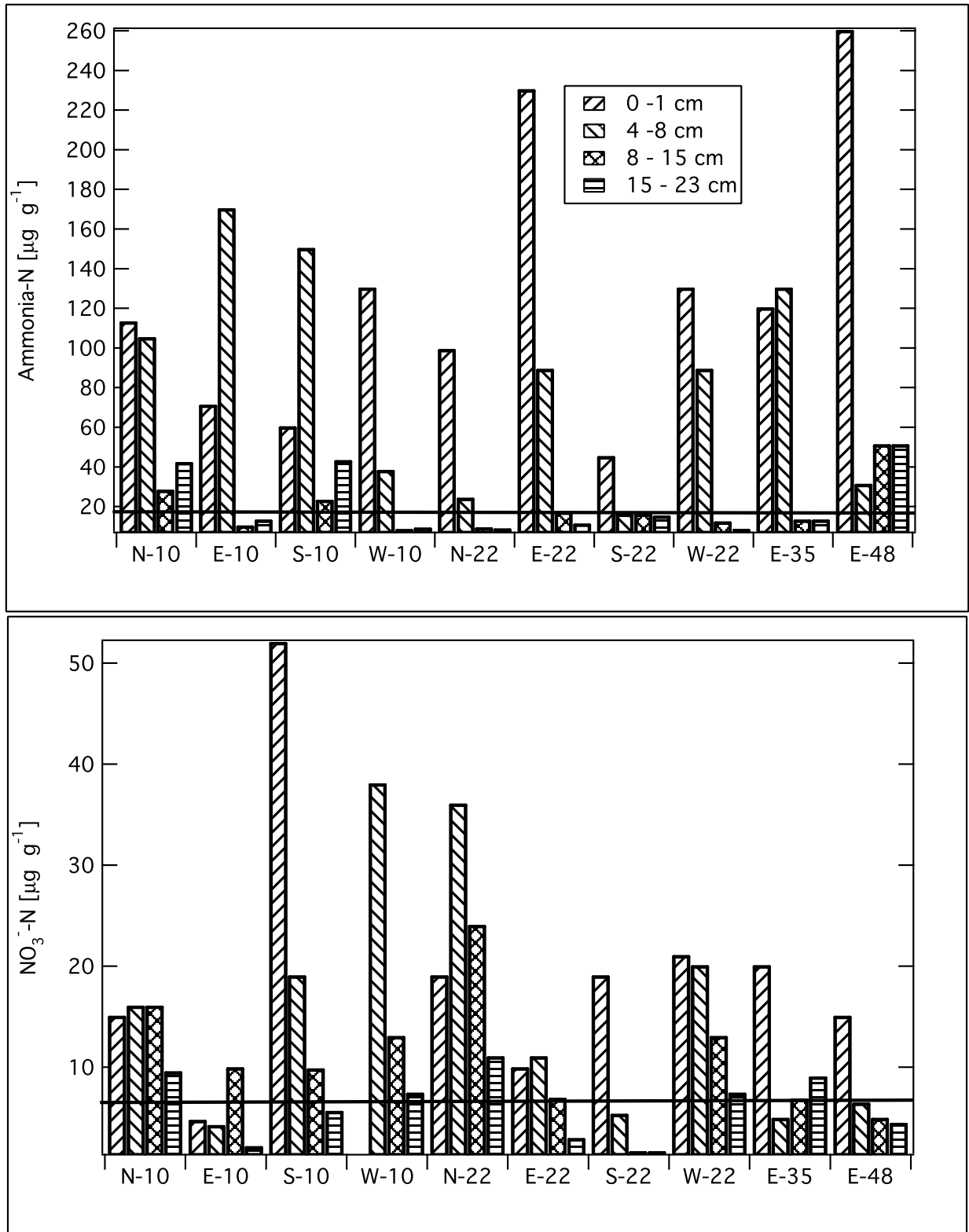


Figure 7.2: Soil ammonia-N (top panel) and NO_3^- -N (bottom panel) concentrations with direction and distance in meters from the sprinkler. Horizontal lines indicate average background levels.

the meteorological data show the wind speed very low and the wind direction blowing away from the measurement path.

One four and a half hour tracer experiment was conducted the day after application. The SF₆ emission and concentration data were used to first determine if the vertical dispersion variables were correct as suggested by Lamb et al., 1995. The suggested dispersion variables overestimated the SF₆ concentrations, this could be due to the close proximity of the line source and the receptors and terrain effects. New dispersion variables were recalculated based upon the tracer data. Due to the fact that there was only one distance from the line source it was not possible to solve for both variables so linear interpolation of the variables suggested by Busse and Zimmerman, 1973 was used to arrive at corrected values based upon wind speed. The emission flux from the tracer experiment average 30 $\mu\text{g m}^{-2} \text{s}^{-1}$ with a standard deviation of 12 $\mu\text{g m}^{-2} \text{s}^{-1}$. The first half hour emissions measurement was 47 $\mu\text{g m}^{-2} \text{s}^{-1}$ and the final measurement was 17 $\mu\text{g m}^{-2} \text{s}^{-1}$.

7.6 Empirical Model

The NH₃ concentration data were averaged for each half hour of the experiment. Data collected when the wind was not directed towards the instrument or the wind deviation greater than 15° were discarded. To calculate the decay in the emissions with time, the revised dispersion variables and the NH₃ concentrations were used in the area source equation to solve for the flux and plotted against time. An exponential equation was fit to the data because Darcy's law for infiltration of a liquid through a soil column exhibits an exponential decay. The empirical equation for the flux from the field is the following

$$NH_3Flux[gm^{-2}s^{-1}] = 9.2e(-6) + 6.7e(-5) * exp(-0.056 * Time[Hours]) \quad (7.11)$$

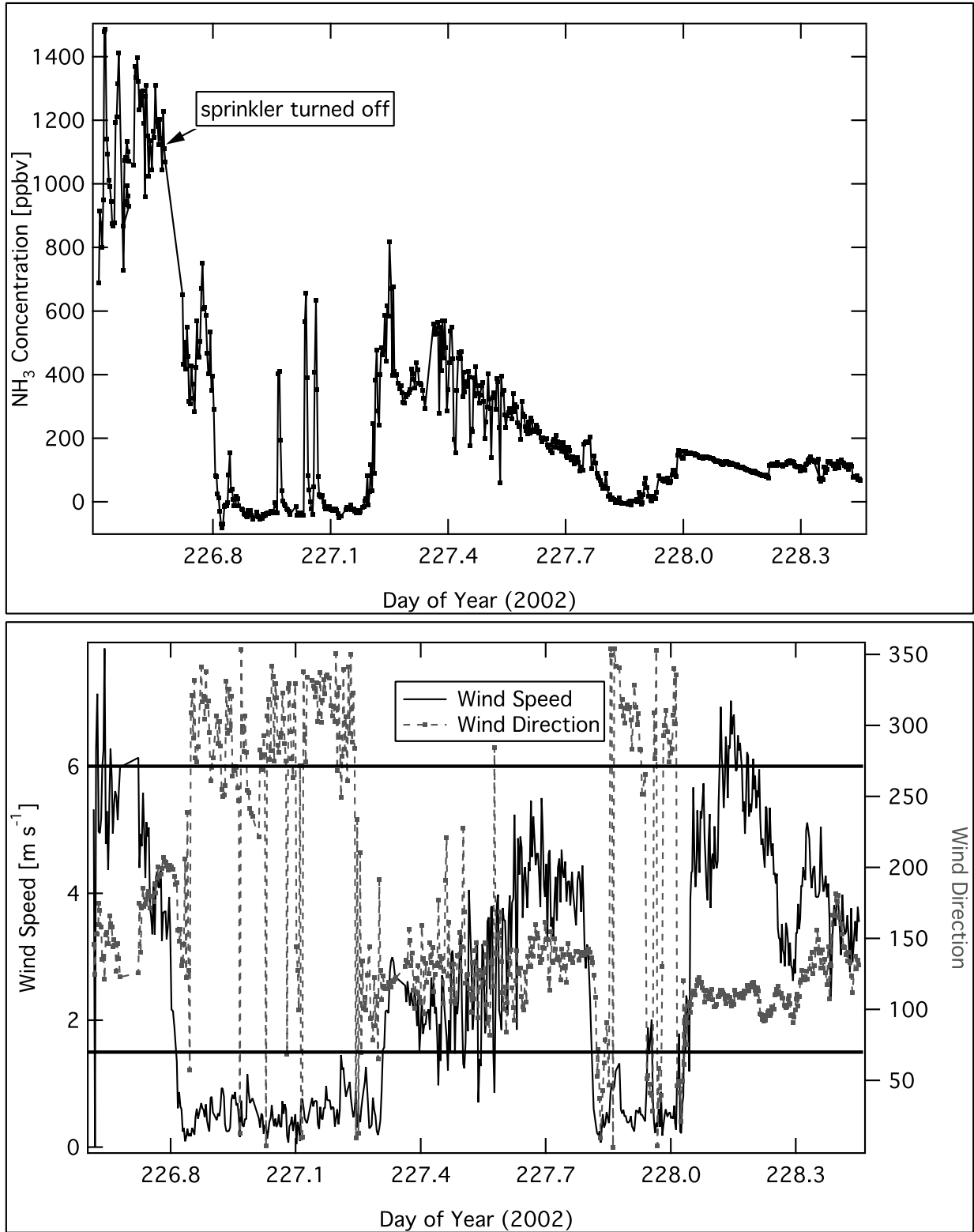


Figure 7.3: NH₃ concentrations (upper panel) and wind speed and wind direction with horizontal bars showing wind directions towards instrument path (lower panel) during the slurry experiment.

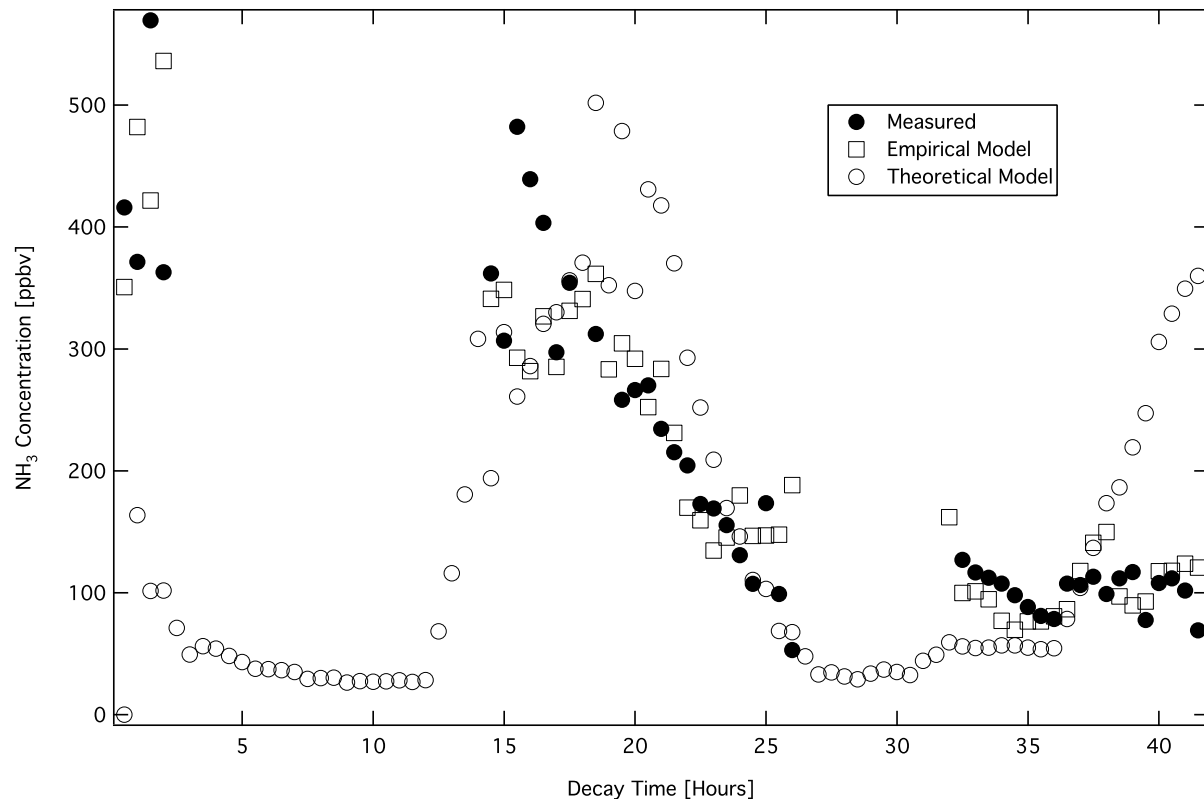


Figure 7.4: Slurry experiment half hour measured concentrations and empirical fit modeled concentrations and theoretical modeled concentrations. Empirical model not run for low wind conditions.

The half hour averaged measured concentration and the empirical model concentration results are shown in Figure 7.4.

7.6.1 Theoretical Model

The theoretical emissions model data were also put into the Gaussian plume area source equation and the estimated downwind concentrations along with the measured concentrations are shown in Figure 7.4. The value of the convective mass transfer coefficient h_m was adjusted until it fit the measurement data, a value of 3.1 was needed. A review of NH₃ models by Ni, 1999 found that the convective mass transfer values for lagoons, buildings, and slurry applied to fields ranged from 1.17×10^{-2} to 1.3×10^{-6} . The higher value of h_m

is due to the canopy limiting transfer to the atmosphere. The model did not predict the initial emissions for the first few hours very well most likely due to slurry on the ground that had not infiltrated. The model did a good job from hours 15 to 26. The model was fairly accurate from hours 32 to 36 but after that over-predicted the concentrations as the temperature increased. This could be due to the slurry forming a crust on the soil and grass as it dried and inhibiting volatilization. The empirical and theoretical models were compared to the measured concentrations to calculate the model errors. The mean bias of the empirical and theoretical models were -0.10 and -11, respectively. The normalized mean bias of the empirical model was -0.050% and for the theoretical model it was -5.4%. The empirical model had a normalized mean error of 22% and for the theoretical model it was 59%.

7.6.2 Total Emissions

To calculate the total emissions and per cow emissions a mass balance approach was used. The WSU dairy has four storage lagoons with a total capacity of 29000 m³. About 2000 m³ of slurry is left in the lagoons at the end of application to use as recycled wash water. It takes one month to empty the lagoons and during that time about another 2000 m³ of waste is added to the lagoons. The total volume of slurry applied to the fields is then 29000 m³. The slurry contains an average ammonia-N concentration 720 mg L⁻¹ times a volume of 29000 m³ gives a total of 21000 kg of ammonia-N to be applied to the fields. Emissions from the sprinkler is 18% of the solution concentration that gives a total sprinkler emissions mass of approximately 4600 kg for the year. For the field emissions slurry is applied to 32000 m² daily and it takes about 30 days to complete the job. Using the empirical model the total emissions for the dairy would be 1300 kg which assuming no nighttime emissions. Using the theoretical model, the total field emissions would be 1000 kg. Combining the sprinkler emissions and the field emissions as modeled by the empirical model the total emissions would be 5900 kg. There are 175 milking cows at the dairy so that is approximately 34 kg

of NH_3 per milking cow for sprinkler application alone.

7.7 Uncertainty Analysis

The total error in total emissions is comprised of two parts, the sprinkler application emissions and the field emissions. Quantifiable error from the sprinkler application derives from the measurement error of the waste from the pump spigot and from the bottles in the field. The error in the liquid analysis calibration is $\pm 5\%$ and the precision of the measurement is $\pm 5\%$. This gives a total error for the sprinkler emissions of $\pm 10\%$. There is an unquantifiable error in the sprinkler application due to the assumption that all of the waste that leaves the sprinkler impacts the field in the application area that makes this estimate conservative. During the experiment no bottle was filled with the expected amount of slurry and during strong wind gusts the waste could be felt about 100 m from the sprinkler. Some of the waste was being transported away from the immediate area and some deposited outside the measurement area.

The error in the tracer ratio method is much more complicated due to the errors in the various parameters of the flux equation. The error in the measurement of the SF_6 emission rate is derived from changes in the flow from the line source due to heating and cooling and errors in measuring the flow from the line source. Duplicate measurements of the flow from the line source gives an error of $\pm 5\%$ and multiple measurements of the flow shows an agreement to within $\pm 2\%$. The combination of these two uncertainties gives the error from the tracer emission rate of $\pm 7\%$. The error in the measurement of the SF_6 is due to calibration errors and the precision of the measurement. The calibration gases used have an accuracy of $\pm 5\%$ and the precision of the measurements is about $\pm 5\%$ for a total error in the SF_6 measurement of $\pm 10\%$.

The uncertainty in the measurement of NH_3 is derived from errors in the NH_3 ultraviolet absorption cross section due to uncertainties in the concentration of the calibration gas. There are also errors in the measurement of the path length, illumination of the spectro-

graph, shifts and stretches of the spectra due to thermal changes in the spectrograph and mathematical errors in the retrieval of the concentration. The overall error is estimated to be $\pm 25\%$ (Mount et al., 2002). Lamb et al., 1995 noted that the error in the dispersion coefficient b is due to uncertainties in the power law estimation of vertical dispersion. The use of experimentally derived values reduced the calculated flux by approximately 20%. The quantifiable error in NH_3 emission flux for the tracer experiment is $\pm 50\%$.

There are a number of systematic unquantifiable errors in the experiment. The tracer flux equation assumes a rectangular area source and uniform emissions. The area covered by the slurry was an oval due to the wind and the amount of slurry applied was not uniform. There were areas where the slurry pooled on the soil surface and other areas where application was minimal. The waste closest to the instrument and thus having the greatest influence on the concentration had the lowest concentration of Ammonia-N in the slurry and the amount applied was less than other areas.

7.8 Conclusions

The dominant emissions from the slurry application with the "Big Gun" sprinkler were from the sprinkler itself, with 18% of the NH_3 in solution volatilizing. Tracer experiment initial emission from the field were $47 \mu\text{g m}^2 \text{s}^{-1}$ and then decreased to $17 \mu\text{g m}^2 \text{s}^{-1}$. An empirical exponential function was fit to the data to model the concentration of slurry at the soil surface, it had a normalized mean bias of -0.050%. A theoretical emissions model was developed based upon the infiltration of slurry into the soil and the subsequent reactions of NH_3 and NH_4^+ in the soil complex, it had a normalized mean bias of -5.4%. Volatilization is related to soil temperature and atmospheric convection at the soil surface so emission reductions can be achieved by applying during cooler temperature and calm winds. The total farm emissions from the sprinkler is 4600 kg with an error of $\pm 10\%$. The annual field emissions derived from the tracer experiment data are estimated to be 1300 kg with an error of $\pm 50\%$. Total emissions for the WSU dairy are approximately 5900 kg or 34 kg NH_3 per

milking cow per year.

Chapter 8

Ammonia Dairy Emissions Model

A Dairy Ammonia Emissions Model for Milking Cow Housing, Waste Lagoons, and
Sprinkler Application

Brian Rumburg, Jack Chen, George H. Mount, Brian Lamb, Hal Westberg, David Yonge

Department of Civil and Environmental Engineering

Ron Kincaid, Kristen Johnson

Department of Animal Sciences

Washington State University

Pullman, Washington 99164-2910

to be submitted to

Atmospheric Environment

8.1 Abstract

Atmospheric ammonia (NH_3) is of concern due to impacts on human health and the environment. This paper describes the development and sensitivity analysis of a meteorological dependent milking dairy cow NH_3 emissions model. The model was developed from measurements made at the Washington State University (WSU) dairy. The model treats emissions for housing, waste storage, and waste application. The WSU dairy has scrape barn housing, anaerobic waste lagoons, and uses sprinklers to apply waste to grass fields. Sensitivity analysis of model input parameters was conducted for annual emissions, average daily emissions, and peak daily emissions. Results from the WSU dairy based upon measured emission algorithms and model runs for a year of meteorological data from the housing, lagoons, and waste application. Emissions are estimated to be 40, 55 and 34 $\text{kg NH}_3 \text{ cow}^{-1} \text{ yr}^{-1}$, respectively. The total annual emissions from the WSU dairy is estimated to be 130 $\text{kg NH}_3 \text{ cow}^{-1} \text{ yr}^{-1}$ which is significantly higher than the EPA NEI estimate of 38 $\text{kg NH}_3 \text{ cow}^{-1} \text{ yr}^{-1}$ based upon European data (EPA, 2004).

The housing emissions module was most sensitive to changes in the pH, a +0.1 change in pH resulted in the model overestimating annual emissions by +30%. The waste storage module was also sensitive to pH changes with a +0.1 change in pH resulting in a +24% change in annual emissions. The waste storage module was also sensitive to the size of the waste storage. Sizing the waste lagoons using literature design criteria the emissions were -29% below the actual lagoon operating conditions. The waste application emissions module for sprinkler application is only sensitive to slurry concentration so any error in estimating slurry will be reflecting in the emissions.

8.2 Introduction

Atmospheric ammonia (NH_3) emissions can impact human health by forming aerosols and can adversely impact the environment when it deposits on sensitive aquatic and terrestrial

ecosystems. Ammonium aerosols are a component of $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 microns) which is a criteria pollutant under the National Air Quality Standard (NAAQS). There are daily and annual standards for $PM_{2.5}$. A study of the historical increases in NH_3 emissions reported emissions estimated less than 10 Tg N yr^{-1} for 1890 and more than 42 Tg N yr^{-1} for 1990 (van Aardenne et al., 2001). Global inventories of NH_3 emissions have reported emissions up to 54 Tg N yr^{-1} with domestic animals excreta being the dominant source (Bouwman et al., 1997).

Estimates of ammonia (NH_3) emissions have historically been on an annual basis because of interest in ammonium sulfate aerosols and their impact on the global radiative balance. Annual emission inventories for NH_3 do not account for meteorology or farming practices that influence emissions (USEPA, 2002). There are seasonal and daily variations in NH_3 emissions due to the physical and biological factors that influence the conversion of organic N to NH_3 and the temperature dependence of the volatilization rate. Current U.S. NH_3 emissions estimates are based upon a limited number of measurements in Europe where farming practices are much different. Bouwman et al., 1997 estimated total N excretions for dairy cattle in North America at 80 kg N yr^{-1} based upon a live weight of 500 kg and a milk production of 15 L day^{-1} . The total NH_3 emissions were estimated to be 25 kg NH_3 yr^{-1} for dairy cows in North American and developed countries, with 62% of the emissions coming from dairy cows in stables and 38% coming from cows in the meadows. The cow assumptions used by Bouwman et al., (1997) are not accurate for the WSU dairy where the average cow weighs 720 kg and produces about 40 L of milk day^{-1} and does not spend any time in a meadow while being milked. Nennich et al., 2005 reported that N excretion was a function of feed intake, protein intake, and body weight. Using the equation developed by Nennich et al., 2005 and the WSU dairy cow data, the daily N excretion is 560 g cow^{-1} day^{-1} with annual N excretions of 200 kg yr^{-1} . Based upon the data from one dairy, the N excretion number used by Bouwman et al., (1997) of 80 kg is low by at least a factor of 2. If emissions are calculated as a percentage of N excreted then emissions will be understated

by at least a factor of 2.

The lack of data in the U.S. has led to large uncertainties in estimates of emission rates, and the factors that influence emissions, which make regulating and mitigating emissions difficult (NRC, 2003). On a per animal basis dairy cows have the largest emissions due to the energy required to make milk.

A dairy cow process model was developed from literature emission rates to improve spatial and temporal dairy cow NH_3 emission estimates (Pinder et al., 2004a). The process model reported annual dairy cow emissions of between 18 and 36 kg NH_3 cow⁻¹ yr⁻¹ (Pinder et al., 2004b). The seasonal variation in NH_3 emissions was estimated using inverse modeling of ammonium (NH_4^+) wet deposition data and it was reported that there were strong seasonal variations in emissions in the eastern U.S. (Gilliland et al., 2003). It was also reported that for 1990 the national emission inventory overestimated emissions by at least 20% (Gilliland et al., 2003). Due to the fast deposition of NH_3 , coarse grid (20 km) modeling of NH_3 deposition does not show the same variability as 5 km grid modeling (Sutton et al., 1998). It was found by Sutton et al. (1998) that it is important to account for the surface-atmosphere exchange instead of using simple deposition velocities to get NH_3 budgets. A sensitivity analysis of NH_3 emissions modeling in the Netherlands reported that the uncertainty in emission factors for dairy cow housing and manure application caused the largest uncertainty in the emission model (Leneman et al., 1998).

Estimating NH_3 emissions is difficult due to the influence of farming practices on emissions and the lack of farming practices information. Since there are multiple interconnected emission sources on a dairy, farming practices can influence emissions in many ways. For example, low housing emissions can lead to higher NH_3 concentrations during waste storage which could lead to greater storage and waste disposal emissions depending upon the practices used. Cow differences should also be accounted for since cow N excretions changes depending upon the diet. Lactating cow N excretion is related to milk production and to dietary N intake (Nennich et al., 2005). Even if milk production is similar, different diets

have been shown to alter the portion of N excreted in the urine or in the manure which can alter the potential for NH_3 emissions (Burgos et al., 2005). Housing, waste handling and storage and waste application methods affect emissions. Using per cow emission estimates does not account for cow or farming differences and could lead to errors in the emissions.

This work is part of a series of papers on the emissions of NH_3 from the milking cows at the Washington State University (WSU) dairy. The purpose is to determine the milking cow emissions and develop an emissions model for use in regional air quality models. The sources measured and modeled include the free stall milking cow housing (Rumburg et al., 2006a), wastewater lagoons (Rumburg et al., 2006b), and the sprinkler application of slurry (Rumburg et al., 2005). For this paper, the objectives were to develop an dairy NH_3 emissions model that calculates hourly emissions for use in regional air quality models and to test the sensitivity of the model against data from the WSU dairy. In addition, the model was designed so that future emissions algorithms for different dairy farming practices can be incorporated in the future. The model also incorporates cow factors influencing N excretions. Model sensitivity evaluated average daily, peak daily, annual average NH_3 emissions from the housing and waste storage modules of the model. This paper discusses the development of the total farm emissions model and the sensitivity analysis.

8.3 Model Development

There are many different dairy farming practices in the U.S. and at this time it is not known how NH_3 emissions vary due to different farming practices. The model was designed so that it can incorporate new emission algorithms for different farming practices based upon a survey of current dairy farming practices. The model was also designed so that individual farm data can be input and farm level emissions can be calculated. The emissions module has three parts: housing, waste storage, and waste application. The model currently only calculates emissions from milking cows. Milking cows are the dominant emission source due to the consumption of protein for milk production. The model consists of a preprocessor

where dietary, cow, and farm information is used to generate a file for the emissions model which uses the preprocessor data and meteorological data to calculate emissions. Currently meteorological dependent emission algorithms developed at the WSU dairy are in the model. The preprocessor where dairy information is input is in an Excel spreadsheet, all the data necessary for the emissions model is then output into a text file to be read by the emissions module coded in Fortran.

8.3.1 WSU Dairy Information

The WSU dairy is located 8 km south of Pullman, Washington USA (N 46° 43.8', W 117° 10.1'). The 175 Holstein milking cows are housed all day in three-sided freestall barns with concrete floors. The waste and used bedding is scraped into waste pits. The pits are flushed with recycled wastewater, the wastewater goes through a solids separator where solids greater than 0.3 cm in diameter are removed. Waste is stored in four lagoons: one high solids settling lagoon, one low solids lagoons and two long term storage lagoons. The two long term storage lagoons are not full the entire year and waste is only added during the fall and winter. A more complete description of the lagoons and the N and solids contents can be found at Neger (2002) and Rumburg et al. (2004). Waste is applied to grass fields using a "Big Gun" spinkler the late summer and early fall.

8.3.2 Milking Cow Housing Emissions Module

Table 8.1 lists the types of dairy cow housing typically found in U.S. dairies based upon a national survey of farming practices (USDA, 2003) and included in the model. The majority percent column is the type of housing used for the majority of cows at the dairy and the used percent reflects dairies using multiple housing types for their cows. The survey results only lists the percentage of dairies responding to the survey and the the number of cows.

Table 8.1: Milking cow housing from USDA (2003) survey of manure handling methods. Majority percent represents where the majority of the cows at each dairy are housed, percent used represents dairies that have multiple housing types for the cows.

Housing Type	Majority Percent	Percent Used
Manure left on Pasture	8.6	72.4
Gutter cleaner	43.4	52.6
Alley Scraper	34.2	51.4
Alley flush with fresh water	0.6	2.5
Alley flush with recycled water	2.1	4.4
Slotted floor	1.1	3.9
Bedded pack	1.1	31.6
Dry lot scraped	7.5	57.0
Other	1.4	3.9

The WSU dairy housing would be classified as an alley scraper. The alley scraper housing emissions algorithm is based upon the algorithms developed by Rumburg et al. (2006a) and briefly described here. The preprocessor calculates dietary intake based upon milk production and cow parameters (NRC, 2001). The model calculates the concentration of N in the urine and the urine volume as described using dietary inputs as described by Bannink et al. (1999). The urea in the urine is calculated by the method reported by Burgos et al. (2005). The model assumes complete conversion of urea to ammonia-N within the model time step. The equation Kamin et al. (1979) was used to determine the partitioning between NH_3 and NH_4^+ in solution based upon the pH. The method of the partitioning of NH_3 between the gas and liquid phases is temperature dependent and was reported by Monteny et al. (1996). The emissions model calculates the flux to the atmosphere based upon the concentration of gaseous NH_3 at the air-liquid interface and the transfer to the atmosphere. The convective mass transfer coefficient was determined empirically using measurement data from the WSU dairy. The model input parameters for the WSU dairy are listed in Table 8.2.

Model sensitivity analysis tested the following model parameters: manure and urine pH, convective mass transfer coefficient, ambient air temperature which was used to simulate the

Table 8.2: WSU dairy information for housing emissions module.

Model Parameter	Value
Number of cows	175
Milk production (kg day ⁻¹)	41
Milk fat (%)	3.4
Dry matter intake (kg day ⁻¹)	26
Dietary crude protein (%)	19
Daily Na intake (g day ⁻¹)	83
Daily K intake (g day ⁻¹)	475
Body weight (kg)	720
Average week of lactation	24
Urine and manure pH	7.8
h_m	0.0038

urine and manure temperature, wind speed threshold, dietary crude protein percent, and milk production.

8.3.3 Waste Storage Emissions Module

Table 8.3 shows the USDA survey of types of waste storage methods used in the U.S.; the majority column shows how the majority of waste on each farm is stored and the percent used column shows the frequency of the different types of manure storage methods. The survey shows that many dairies use multiple manure handling methods. The WSU dairy uses earthen basins or lagoons and solids composting.

Waste storage emissions are a function of surface area so the larger the volume of waste that needs to be stored the larger the surface area. Storage time also is important to determining waste application timing. Dairies with small storage capacities must dispose of waste more frequently than those dairies with larger storage capacities. In some areas waste application is not possible in the winter due to frozen soil or possible contamination of sensitive nearby waterways.

Table 8.3: National survey results of waste storage practices in the U.S. . The majority percent column is how the majority of the waste on the farm is stored and the percent used column represents the usage of different types of waste storage (USDA, 2003).

Waste Storage Type	Majority Percent	Percent Used
Stored in manure spreader	40.8	51.0
Below floor slurry or deep pit	6.1	11.5
Slurry stored in tank	7.6	10.7
Slurry stored in earthen basin and not treated	22.5	26.1
Treatment lagoon	4.6	7.3
Manure pack (inside barn)	2.0	48.1
Outside storage for solid manure not in a dry lot	9.9	32.6
Outside storage for solid manure within a dry lot	4.0	18.2
Stored solid manure in a building	0.9	2.3
Stored solid manure with picket dam	1.3	3.3
Composted	0.3	4.3
Collection of methane/biogas	0.0	0.3
Other	0.0	0.2

Table 8.4: Maximum dairy waste storage times in the U.S.. (USDA, 2003).

Capacity	Percent
Less than 7 days	31.4
7 to 29 days	7.4
30 to 59 days	6.7
60 to 89 days	5.2
90 to 179 days	10.7
180 to 364 days	24.9
365 days or more	13.7

The lagoon emissions module is based upon the mechanistic model described by Rumburg et al. (2006b). The model calculates emissions based upon the lagoon ammonia-N (NH_4^+ and NH_3) concentrations, temperature, lagoon pH, wind speed threshold, and convective mass transfer coefficient. The inputs to the model include: ammonia-N concentration, pH, threshold wind speed threshold below which there is no transfer to the bulk atmosphere and lagoon size. For the WSU dairy, the lagoon concentration is temperature dependent due to bacterial ammonification so the ammonia-N concentration is set so that there is a threshold temperature and the concentration above and below that temperature can be entered. For the WSU dairy below 10° C the ammonia-N concentration is 530 mg L⁻¹ and above it was 660 mg L⁻¹. The lagoon was also assumed to be frozen at temperatures below -3° C. The annual measured pH of the WSU lagoon is 7.8. For WSU dairy, the lagoon size is known, but lagoon sizes are not always known. Waste storage size can be estimated based upon American Society of Agricultural Engineers design criteria (ASAE, 1992). The preprocessor calculates lagoon size based upon input values of the storage period for the waste and the design depth; the model assumes one large lagoon. Freezing point, convective mass transfer coefficient and threshold wind speed can also be input. The convective mass transfer coefficient for the WSU dairy lagoons was determined to be 5.8×10^{-4} (Rumburg et al., 2006b). The wind speed threshold where there was no transfer of NH_3 to the bulk atmosphere was set at 1.5 m s⁻¹.

8.3.4 Waste Application Module

Table 8.5 shows the majority of application types used. The percentages do not add up to 100% because some dairies use multiple methods of waste application. The WSU dairy uses sprinkler application for the slurry waste, solids are removed using a solids separator and are composted. Some of the composted solids are used for bedding and the rest is sold commercially. The dairy normally applies waste to the fields during the late summer and early fall.

Table 8.5: USDA survey of application types used. Numbers do not add up to 100% due to some dairies using multiple methods of waste application.

Method	Percent
Broadcast/solid spreader	90.0
Surface application by tank truck	30.1
Subsurface injection	6.1
Irrigation/sprinkler	7.6
Other	0.3

The sprinkler waste application module is comprised of two parts: emissions from the sprinkler and emissions from the field after application. During one experiment, Rumburg et al. (2005) reported that 18% of the ammonia-N volatilized during sprinkler application. An empirical equation was developed to model emissions decay with time and a theoretical emissions equation was also developed (Rumburg et al., 2005). The field emissions model used output from a groundwater model to simulate diffusion of the slurry through the soil. Soil temperature was also modeled using a canopy and radiation model. Due to the specifics of each of these models, an empirical model was also developed for use in the NH₃ emissions model. Annual sprinkler emissions were 4600 kg while field emissions were only 1300 kg. Since sprinkler emissions are the dominant source of emissions from application only that was tested. The model assumes that 18% of the ammonia-N in the slurry will volatilize. Emissions will directly scale with ammonia-N concentration and the volume of waste applied.

8.4 Results

8.4.1 Housing Emissions

The stalls sensitivity analysis is shown in Table 8.6. The base case is the actual conditions for the WSU and the percent change columns are the percent change from the base case. Annual, average and peak daily emissions and daily standard deviations were evaluated. The WSU emissions model calculated annual NH₃ emissions at 7000 kg yr⁻¹ and a mass balance check of emissions calculated maximum emissions of 7900 kg yr⁻¹ (Rumburg et al.,

2006a). The model was most sensitive to over estimating the pH of the manure and urine on the housing floor. A +0.2 pH change resulted in annual emissions and peak daily emissions being almost 2 times the base case. Even a +0.1 change in the pH resulted in a base case deviation on the order of 30% for annual, average and peak daily emissions. A -0.2 change in the pH resulted in a base case deviation of about -45% in annual, average and peak daily emissions. A +25% change in the h_m had an emission base case deviation of 30% and an under estimation of h_m -25% had an base case deviation of 20%. Model base case deviations were 21% for air temperature errors of $\pm 2^\circ$ C. Choosing the wind speed threshold where the ambient wind speed are strong enough so that there is mass transfer at the housing floor surface is difficult. Buildings and other obstructions can significantly reduce the ambient wind speed. Changing the threshold wind speed from 1 m s^{-1} to 2 m s^{-1} resulted in annual emissions being underestimated by 43% and average daily emissions by -45% compared to the base case. Peak daily emissions were only reduced by -15%. Increasing the CP from 19% to 21% resulted in a than 20% base case deviation in annual, daily and peak daily emissions. Reducing CP to 15% under estimated annual emissions 21%, suggesting emissions can be reduced somewhat from feeding a lower protein diet. Increasing milk production to 50 kg day^{-1} increased emissions by a maximum of 13% and reducing milk production resulted in a model error of less 6%. The model was most sensitive to changes in the pH of the urine and manure and the convective mass transfer coefficient.

8.4.2 Lagoon Emissions Module

The lagoon emissions model sensitivity analysis is shown in Table 8.7 with the base case being the actual WSU dairy lagoon conditions. As with housing, the model is very sensitive to changes in the pH. A +0.2 change in pH from the base case results in a +75% deviation in annual emissions while a -0.2 change in pH has a -45% deviation in the base case for annual emissions. A $\pm 50\%$ change in the h_m had a base case deviation of about $\pm 45\%$ for annual

Table 8.6: Housing emissions model sensitivity analysis. Base case conditions, milk production 41 kg day⁻¹, crude protein (CP) equals 19%, pH = 7.8, $h_m = 5.8 \times 10^{-4}$, ambient air temperature, and a wind speed threshold where there is no transfer to the bulk atmosphere of 1 m⁻¹.

Model Base Case Deviation	Annual Emissions (kg yr ⁻¹)	Percent Change	Average Daily (kg d ⁻¹)	Percent Change	Peak Daily (kg d ⁻¹)	Percent Change (kg d ⁻¹)	Daily Std. Dev. (kg d ⁻¹)
Base Case	7000	-	20	-	86	-	17
pH = 8.1	14000	100	40	100	170	98	32
pH = 7.9	9200	31	26	30	110	28	25
pH = 7.7	5900	-16	17	-15	73	-15	14
pH = 7.5	3700	-47	10	-45	47	-45	8.8
$h_m + 50\%$	11000	57	31	55	140	63	26
$h_m + 25\%$	9200	31	26	30	110	28	21
$h_m - 25\%$	5500	-21	16	-20	68	-21	13
$h_m - 50\%$	3700	-47	14	-30	45	-48	8.6
Air Temp + 5°C	10000	43	30	50	120	39	23
Air Temp + 2°C	8500	21	24	20	100	16	19
Air Temp - 2°C	6400	-8.6	18	-10	80	-7.0	15
Air Temp - 5°C	5100	-27	15	-25	66	-23	12
WS Thrshld 2 m s ⁻¹	4000	-43	11	-45	73	-15	14
WS Thrshld 1.5 m s ⁻¹	5600	-20	16	-20	82	-4.7	16
WS Thrshld 0.5 m s ⁻¹	8700	24	25	25	100	16	18
WS Thrshld 0 m s ⁻¹	9900	41	28	40	100	16	19
CP = 21%	8300	19	23	15	100	16	19
CP = 17%	6500	-7.1	18	-10	80	-7.0	15
CP = 15%	5500	-21	16	-20	68	-21	13
MP 50 kg day ⁻¹	7900	13	22	10	97	13	16
MP 45 kg day ⁻¹	7600	8.6	22	10	94	9.3	17
MP 35 kg day ⁻¹	7000	0	20	0	86	0	18
MP 30 kg day ⁻¹	6800	-2.9	19	-5.0	83	-3.5	19

emissions. The model was also sensitive to the wind speed threshold, increasing the threshold to 2 m s^{-1} from 1.5 m s^{-1} resulted in the model under predicting annual emissions by -29% compared to the base case. Choosing a wind speed threshold is difficult due to disturbance in the wind field. The WSU dairy has a berm around the lagoon that is at least 1 m above the lagoon surface and other local factors such as trees could also disturb the wind field so that the wind speed at the lagoon surface is not strong enough to transfer the NH_3 to the bulk atmosphere. A base case deviation of over or under estimating the lagoon ammonia-N concentration had an error on the order of the error in the over or under estimation. Using the literature design criteria to estimate lagoon size under estimated annual emissions by -29% and average daily and peak daily emissions by -32 and -33%, respectively compared to the base case. The WSU lagoons are shallow due to a low water table so the error in estimating the lagoon depth led to the error.

8.4.3 Waste Application Emissions

The waste application emission module has two components. The sprinkler emissions and the field emissions. Sprinkler emissions were found to be 18% of the ammonia-N of the slurry applied (Rumburg et al., 2005). Since only one useable experiment was conducted for the slurry application temperature or wind dependence of emissions was not determined. Therefore, the emissions are 18% of the slurry ammonia-N input. For the WSU dairy the waste applied had an average ammonia-N concentration of 720 mg L^{-1} . This is higher than the concentration of the main lagoon due to solids at the lagoon bottom being mixed into solution prior to field application. For field emissions an empirical equation based upon the time after initial application.

Any error in estimation of the ammonia-N concentration will result in a corresponding error in the emissions. Estimating the timing of waste application is the largest source of error. Dairies apply waste depending upon if their storage is full, the best time to fertilize

Table 8.7: Lagoon emissions model sensitivity analysis. Base case conditions are 4 lagoons with 2 used as storage during part of the year, TAN concentration of 660 mg L⁻¹ for temperatures above 10 ° C and 530 mg L⁻¹ for temperature below that, pH = 7.8, $h_m = 0.00058$, ambient air temperature, wind speed threshold below which there is no mass transfer to the atmosphere of 1.5 m s⁻¹.

Model Base Case Deviation	Annual Emissions (kg yr ⁻¹)	Percent Change	Average Daily (kg d ⁻¹)	Percent Change	Peak Daily (kg d ⁻¹)	Percent Change	Daily Std. Dev. (kg d ⁻¹)
Base Case	9700	-	28	-	110	-	24
pH = 8.1	17000	75	48	71	190	73	40
pH = 7.9	12000	24	33	18	130	18	29
pH = 7.7	8000	-17	23	-18	90	-18	20
pH = 7.5	5300	-45	15	-46	62	-44	14
$h_m + 50\%$	14000	44	39	39	150	36	33
$h_m + 25\%$	12000	24	33	18	130	18	29
$h_m - 25\%$	7600	-22	21	-25	86	-22	19
$h_m - 50\%$	5200	-46	15	-46	62	-44	14
WS Thrshld 2 m s ⁻¹	6900	-29	20	-29	97	-12	22
WS Thrshld 1.0 m s ⁻¹	13000	34	37	32	120	9.1	27
WS Thrshld 0.5 m s ⁻¹	15000	55	44	57	150	36	31
WS Thrshld 0 m s ⁻¹	17000	75	48	71	160	46	34
Air Temp + 5°C	13000	34	38	29	140	27	31
Air Temp + 2°C	11000	13	31	11	120	9.1	27
Air Temp - 2°C	8600	-11	25	-11	97	-12	22
Air Temp - 5°C	7200	-26	20	-29	82	-26	19
Ammonia-N + 25%	12000	24	33	18	130	18	29
Ammonia-N + 10%	11000	13	30	7.1	120	9.1	26
Ammonia-N -10%	8900	-8.2	25	-11	100	-9.1	22
Ammonia-N -25%	7600	-22	21	-25	86	-22	19
Lagoon Design (8100 m ²)	6900	-29	19	-32	74	-33	21
Lagoon Design + 50%	10000	3.1	28	0.0	110	0.0	29
Lagoon Design + 25%	8600	-11	24	-14	93	-16	25
Lagoon Design - 25%	5200	-46	14	-50	56	-49	17
Lagoon Design - 50%	3400	-65	9.4	-66	37	-66	14

the crops and other factors.

8.5 Conclusions

A dairy emissions model was developed to estimate NH_3 emissions from milking dairy cows at hourly intervals based upon dairy farming practices and meteorological conditions. The model has three modules to calculate emissions from housing, waste storage, and sprinkler application. Currently the model has housing emission algorithms for a scrape barn, waste storage emission algorithms for earthen waste lagoons, and waste application emission algorithms for sprinkler application.

Model sensitivity analysis was run on the housing and on the lagoon modules and compared to the base case of emissions developed for the operating conditions at the WSU dairy. For the base case annual NH_3 housing emissions were 40 kg, waste lagoon emissions were 55 kg and waste application emissions were 34 kg for a total of 130 kg NH_3 cow⁻¹ yr⁻¹.

The housing model was most sensitive to raising the pH of the manure and urine in the stalls. A +0.3 change in the pH of the manure and urine from the base case resulted in annual emissions being doubled. A base case deviation of +50% in the convective mass transfer coefficient resulted in the model over estimating annual emissions by +57%. The model had an base case deviation of less than 20% for changes in the CP ranging from 15 to 21% of the feed.

The lagoon model was also sensitive to pH. The base case deviation of +75% was observed for a +0.3 change in the lagoon pH. The base case deviation in the annual emissions for the convective mass transfer coefficient was approximately the percentage of the change to the mass transfer coefficient. Simulating the WSU dairy lagoon based upon literature design criteria the model had a base case deviation of -29%. Estimating lagoon size is a potential source of error in the model.

Sensitivity analysis was not conducted on the waste application module. The model calculates sprinkler emissions as a function of slurry concentration so any error in estimating

slurry concentration will be reflected in the emissions. The field emissions module is empirical and only a function of time from initial application.

Chapter 9

Conclusions and Future Work

9.1 Conclusions

There is a growing interest in the increasing anthropogenic NH_3 emissions due to concerns about impacts on human health and the environment. Emissions in the U.S. are not well understood due to a lack of measurement data from the largest source, domesticated animals. To address the lack of NH_3 emissions data, the WSU dairy ammonia emissions project was conducted.

The major sources of NH_3 emissions from dairies are the housing area, waste storage, and waste application. Housing emissions are the result of the fast reaction of urea in the urine with the enzyme urease in the manure to form ammonia-N and the subsequent volatilization of NH_3 . The causes of waste storage emissions are similar to housing emissions but there is additional ammonia-N due to the anaerobic bacterial breakdown of organic N in the waste. Waste application emissions occur when the waste is exposed to the air during application and the volatilization from the field after application.

Short-path DOAS was shown to be a very effective way to make fast and accurate measurements NH_3 without measurement artifacts. The DOAS NH_3 concentration data coupled with the tracer ratio method flux technique worked well for measuring fluxes from the emission sources at the dairy. These measured emissions are much larger than normally assumed. This work has also produced emission algorithms for predicting NH_3 emissions from dairies based upon the physical and chemical factors influencing emissions. These emissions models predict much larger emissions than previously assumed. Due to the complexity of dairy farming, more work is needed to understand dairy emissions from the housing areas, waste lagoons, and waste application for different dairy farming methods to make the derived models truly applicable within a region.

9.1.1 Housing Emissions

The current U.S. dairy cow housing emissions estimates are based upon a limited number of measurements made in Europe where dairy housing farming practices are much different from the U.S.. Slatted floor housing is common in Europe (Pollet et al., 1998) but not common in the U.S. (USDA, 2002). Slatted floor housing catches the waste in pits below the cows, the pits reduce emissions due to the reduced wind speed at the waste surface reducing mass transfer to the bulk atmosphere. Housing emissions estimates also do not take into account temperature effects or the amount of N excreted by the cows. Dairy cow research has shown a correlation between milk production, cow weight, N intake and N excreted and that also is not factored into current emissions estimates. Thus, there is a large uncertainty in U.S. dairy NH_3 housing emission estimates. The goal of this project was to measure dairy cow housing emission rates and develop an emissions model.

During this project, two tracer ratio flux methods were used to measure emissions from the milking cow housing. The average flux using a line source techniques was 8.1 ± 5.2 $\text{mg cow}^{-1} \text{ s}^{-1}$ at an average temperature of 18° C . The average flux derived from a point source tracer was 4.6 ± 1.2 $\text{mg m}^{-2} \text{ s}^{-1}$ at an average temperature of 14° C . The difference in emissions is partly due to temperature differences.

The release of NH_3 to the atmosphere was modeled using a mechanistic model of chemical and physical conditions and a Gaussian plume model calibrated with the tracer gas data. The combined model had a normalized mean error of $\pm 30\%$ when compared to measured concentrations. The model was very sensitive to changes in the pH and less sensitive to temperature. The model was not very sensitive to changes in crude protein or milk production. The emission model was run for a year and annual emissions were calculated to be $7000 \text{ kg } \text{NH}_3$ ($40 \pm 12 \text{ kg cow}^{-1} \text{ yr}^{-1}$) which is in excellent agreement with a N mass balance maximum of 7900 kg . Housing emissions for the entire dairy of 175 milking cows were seasonal and ranged from about $10 \text{ kg } \text{NH}_3 \text{ day}^{-1}$ in the winter to over $80 \text{ kg } \text{NH}_3 \text{ day}^{-1}$ in the summer.

Measurements of NH_3 fluxes from the WSU dairy and the development of a cow N excretion model coupled to a mechanistic emissions model significantly improves the understanding of emissions from dairy cow scrape barn housing in the U.S..

The coupling of the cow excretion model with the mechanistic emissions model reduces the error in dairy housing NH_3 emissions since factors such as diet and milk production are accounted for. The model error is also reduced since the temperature dependence of emissions is taken into consideration. Sensitivity analysis showed that the pH of the manure and urine mixture is the most important factor in model accuracy and lowering the pH of the urine and manure has the greatest potential to lower NH_3 housing emissions. Using the housing emissions model and total N excretions it is possible to calculate the amount of N in waste storage for use in waste storage emissions.

9.1.2 Lagoon Emissions

Compared to swine lagoons little research has been done on NH_3 emissions from dairy lagoons. As a result, the EPA recently started using swine lagoon data to estimate dairy lagoon emissions (EPA, 2004). No research has been done comparing the swine and dairy lagoon emissions. Empirical models of swine lagoon emissions have been developed that have ammonia-N concentration and temperature dependence but models for dairy lagoons have not been developed. As a result, dairy lagoon emissions are very uncertain. Reducing dairy lagoon emissions is possible and one way is by the aerobic treatment of the waste, but no data is available on the effectiveness of commercial aerators reducing dairy lagoon NH_3 emissions.

Concentration measurements of NH_3 were made downwind of the low solids lagoon at the WSU dairy. Ammonia emissions from tracer ratio flux measurements ranged from 30 to $150 \mu\text{g m}^{-2} \text{s}^{-1}$ depending upon temperature. The tracer ratio experiments were also used to calibrate a Gaussian plume model of NH_3 transport. A theoretical emissions model was developed based upon lagoon ammonia-N concentrations and chemistry. This theoretical

emissions model and the calibrated plume model predicted the downwind concentrations of NH_3 best when using the air temperature, not the lagoon temperature. The normalized mean error of the model using ambient air temperature as the lagoon temperature input was 21%. The model is very sensitive to changes in pH. The daily lagoon fluxes ranged from over 100 kg per day in the summer to 0 when the lagoon was frozen. The annual emissions were calculated to be 9700 kg or $(55 \pm 11 \text{ kg cow}^{-1} \text{ yr}^{-1})$ based upon normal dairy lagoon operating conditions.

As a test of mitigation strategies, two commercial aerators were run continuously from July 30 to August 28, 2001. No detectable change in liquid ammonia-N concentration and no detectable levels of dissolved oxygen were found throughout the experiment which indicates that the aerators failed to introduce enough oxygen into the lagoon to biologically degrade the NH_3 . Aqueous N and total and volatile solids concentrations at 0.90 m decreased in concentrations due to mixing with the water column, but samples at a depth of 0.15 m did not increase indicating that the aerators were not mixing the entire sludge layer from the bottom of the lagoon into the entire water column. The aerators eventually created large islands of sludge around them limiting their mixing ability. There was no detectable change in atmospheric NH_3 downwind of the lagoon during the experiment confirming the liquid analysis. The average atmospheric NH_3 concentration 50 m downwind of the lagoon was about 300 ppbv throughout the entire experiment.

Measurements of liquid ammonia-N concentrations from a dairy lagoon show that bacterial ammonification is temperature dependent and can influence downwind NH_3 concentrations. Lagoon fluxes were also shown to be temperature dependent. A lagoon emissions model was developed that accounts for the effects of temperature, pH, bacterial ammonification rate, and ammonia-N concentration. Since the model accounts for the physical and chemical parameters involved in NH_3 emissions it can be used for many different lagoon operating conditions. The lagoon pH was shown to be the most sensitive model input in modeling NH_3 emissions accurately. This project has also tested low power commercial aera-

tors and shown that they are not effective at introducing enough oxygen into the WSU dairy lagoon to reduced lagoon ammonia-N concentrations or downwind NH_3 concentrations. The treatment of lagoon waste is not only important in reducing waste storage emissions but can also reduce waste application emissions.

9.1.3 Waste Application Emissions

No measurements of NH_3 emissions from a "Big Gun" sprinkler slurry application have been reported in the literature and very few measurements of dairy waste application to grass fields have been reported. The NH_3 emission rate from sprinkler application and field volatilization is not known despite the use of this common technique in the U.S. to dispose of dairy waste. Models of volatilization of NH_3 have shown that emissions decay with time due to infiltration of the slurry into the soil and binding to soil particles. These models are not suitable for air quality modeling due to their complexity so further measurements and modeling are needed.

The dominant emissions from the slurry application with the "Big Gun" sprinkler were measured to be from the sprinkler itself, with 18% of the NH_3 in solution volatilizing. Initial emission from the field were $47 \mu\text{g m}^2 \text{s}^{-1}$ which decreased to $17 \mu\text{g m}^2 \text{s}^{-1}$ in four and a half hours. An empirical exponential function was fit to the emissions data to model the concentration of slurry at the soil surface, and a theoretical emissions model was developed based upon the infiltration of slurry into the soil and the subsequent reactions of NH_3 and NH_4^+ in the soil complex. Volatilization from the soil is related to soil ammonia-N concentration, soil temperature and atmospheric convection at the soil surface. Emission reductions are possible by applying to fields during cooler temperatures and calm winds. The total WSU dairy waste application emissions from the sprinkler is 4600 kg with an error of $\pm 10\%$. The annual field emissions derived from the tracer experiment data are estimated to be 1300 kg with an error of $\pm 50\%$. Total waste application emissions for the WSU dairy are approximately 5900 kg or $34 \pm 6 \text{ kg NH}_3$ per milking cow per year.

The measurement of NH_3 emissions from a "Big Gun" sprinkler showed that emissions were ammonia-N concentration dependent. A theoretical model of field emissions showed that the crop canopy limits emissions by lowering the temperature of the soil and by limiting mass transfer to the bulk atmosphere. A simple exponential function was shown to model NH_3 field emissions and can be used effectively by air quality models. Coupled together the housing, lagoon, and waste application, models can be used to determine overall dairy farm emissions.

9.1.4 WSU Dairy Emissions Model

Previous total dairy NH_3 emissions models used annual emission estimates to model NH_3 emissions and did not account for the influence of meteorology, farming practices, or cow differences. Estimates of U.S. NH_3 emissions are currently based upon a few European measurements where farming practices are much different. This work shows that European annual emissions are very low compared to the data from the WSU dairy. Using the annual European emissions data for air quality models will not accurately predict concentrations or deposition.

A total dairy emissions model was developed to estimate NH_3 emissions from the WSU milking dairy cows at hourly intervals based upon dairy farming practices and meteorological conditions. The model has three modules to calculate emissions from housing, waste lagoons and sprinkler application. Only emission algorithms for a scrape barn, earthen waste lagoons, and sprinkler application are currently in the model. The annual per cow emissions were estimated based upon measured emission algorithms and model runs for a year of meteorological data from the housing, lagoons, and waste application as shown in Table 9.1. The mass balance and emissions are in good agreement. The EPA NEI estimate of 38 kg NH_3 cow⁻¹ yr⁻¹ based upon European data (EPA, 2004).

Model sensitivity analyses were run on the housing and on the lagoon modules. The

Table 9.1: Annual NH₃ emissions from the WSU dairy by source. Housing emissions uncertainties are based upon comparison to measurements and are 30% and lagoon emissions are also based up measurements and the uncertainty is 20%, waste application errors are based upon measurement error and are 10% for the sprinkler and 50% for the field emissions. Nitrogen mass balance numbers are based upon measurements and an estimated uncertainty of 20%. The waste application sprinkler emissions are based upon the mass balance so the numbers are the same. Mass balance field calculations were not possible.

Emission Source	Modeled kg NH ₃ yr ⁻¹	N Mass Balance kg NH ₃ yr ⁻¹	Per Cow kg NH ₃ yr ⁻¹
Housing	7000 ± 2100	7900 ± 1600	40 ±
Lagoons	9700 ± 1900	9300 ± 1900	55 ±
Waste Application - Sprinkler	4600 ± 460	4600 ± 460	27 ±
Waste Application - Fields	1300 ± 600		7 ±
Total	23000 ± 5000		130

housing model was most sensitive to changes in the pH of the manure and urine in the stalls. A +0.3 pH deviation from the base case for the manure and urine resulted in annual emissions being doubled. An base case deviation of +50% in the convective mass transfer coefficient resulted in the model over estimating annual emissions by +57%. The model results had a less than 20% deviation for changes in the CP of the feed or the milk production. The lagoon model was also sensitive to pH. The deviation from the base case was +75% in emissions for a pH change of +0.3. The change in the annual emissions for the convective mass transfer coefficient was approximately the percentage of the over or under change in the convective mass transfer coefficient. Simulating the surface area of the WSU dairy lagoons based upon literature design criteria the model had a base case deviation of -29%. The only input parameter for the waste application emissions module is the concentration of the ammonia-N of the waste being applied and emissions

A dairy emissions model was developed based upon measurements at a U.S. dairy that depends upon meteorology, farming practices, and cow differences. Model input sensitivity analysis showed that the most important factor in predicting emissions is the pH of the housing waste and the lagoons and the ammonia-N concentration for sprinkler waste application. The model was designed so that different farming practices can be added in the future to improve the model performance.

Modeled annual NH_3 housing emissions were 40 kg, waste lagoon emissions were 55 kg, and waste application emissions were 34 kg for a total of 130 kg NH_3 cow^{-1} yr^{-1} . Confidence is gained in this number since a total dairy N balance based upon inputs and outputs of N gives similar results. The EPA is currently estimating dairy cow emissions at 38 kg NH_3 cow^{-1} yr^{-1} based upon European data (EPA, 2004). Differences in farming practices and increased N excretions based upon higher milk production levels are most likely the reason for the large differences in emissions.

Further research in the U.S. is needed on the different dairy farming practices so that model accuracy can be improved. Modeling of dairy NH_3 emissions is needed to determine if dairy NH_3 emissions are a significant risk to human health and environmental quality.

9.2 Future Work

9.2.1 Washington State Dairy Emissions

There are many unknowns concerning NH_3 emissions from dairies and their impact on air quality in the state of Washington. Using the WSU dairy NH_3 emissions model to estimate emissions from all state dairies assumes that WSU dairy emissions are typical of dairies in the state. There are many different dairy farming practices in the state and the effects of different farming practices on emissions is unknown at this time. Despite the uncertainty the WSU NH_3 emissions model needs to be run for all dairies in the state to determine if dairies are significantly affecting the air quality. If dairies are a significant part of the problem then a survey of dairies in the area is needed to understand if using the WSU dairy to represent all dairies is justified. If farming practices are determined to be significantly different then more measurements will be needed. Measurements of NH_3 and other factors influencing emissions need to be made over a sufficiently long time period so that the temperature dependence of emissions is determined.

Improvements to the understanding of the chemical reactions involved in the production

of NH_3 are needed. For housing emissions, understanding the pH of the urine and manure mixture is needed. Measuring the Henry's law constant for the manure and urine mixture would be helpful since currently a Henry's law constant for NH_3 in water is being used. Investigation into the mitigation of NH_3 emissions could be achieved by changing the cow diet to reduce the pH of the urine patches in the stalls and in the lagoons and reducing the protein in the diet. Alternative housing options such as slatted floor and dry lots need to be studied.

Lagoon emissions are controlled by the Henry's law constant and there are large uncertainties in using NH_3 in water Henry's law constants. The temperature dependence of the bacterial ammonification rate is needed to improve the model. Sampling of typical dairy lagoons for ammonia-N, TKN, and pH values would help in understanding the range of lagoon operating conditions.

Another opportunity for research is designing surface aerators to turn dairy waste lagoon into facultative lagoons. Initial design could be done in the laboratory and tested at the WSU dairy. Investigation of the pH buffering capacity of the lagoon would be helpful to understand the range of pH values found in lagoons.

Waste application is an area that needs significantly research due to the many variables involved, including application method, type of crop applied to, soil type, slurry characteristics, and temperature. Theoretical slurry application models of waste application are most likely not useful due to the need to model soil temperatures and slurry infiltration and possibly plant uptake. A state survey of the types and times and amounts of application would help understand what types of application need to be studied. The rate of soil infiltration of slurry needs to be studied along with the binding of NH_4^+ to the different soil types. The rate of plant uptake of NH_3 in applied waste needs investigation.

A possible improvement to the flux measurement would be modifying the instrument from an short-path to an open air multi-pass cell. In combination with a sonic anemometer, this would allow for the instrument to make disjunct eddy correlation flux measurements at

all times. The Xe lamp could be directed to a fiber optic and then into the cell and the cell output could be directed to the spectrograph. The DOAS measurement could not run at 10 Hz for eddy correlation flux measurements but could make a measurement at least every second depending upon the needed path length and the mirror and fiber optic losses. The use of a disjunct eddy correlation method would reduce some of the errors involved in the tracer ratio method and would allow for continuous flux measurements.

9.2.2 WSU Dairy Ammonia Emissions Reduction

Reducing emissions from the WSU dairy is possible and the dairy is an ideal for further research into testing different emission reduction strategies since baseline emissions data has already been determined.

Housing emissions are difficult to reduce since emissions start occurring almost immediately after the urine is voided; but dietary changes could be made to reduce the pH of the urine and also reduce the N in the diet. The focus should be first on reducing the pH of the urine and manure. Urease inhibitors could be also tested to determine how effective they are and the impact on N concentrations in the lagoons. The cost might be prohibitive and the impacts of the urease inhibitor on the lagoon chemistry needs to be determined. Slatted floors are used in Europe to reduce emissions, a small scale slatted floor experiment could be conducted to compare emissions. The advantage of the slatted floor is that the surface area where the urea and urease react is reduced and in the pit below the cows the mass transfer to the atmosphere is reduced provided that the air flow at the liquid-air interface was low. Any change to the housing system would require studying the lagoon and waste application to determine if any emissions reductions were increasing emissions somewhere else.

Lagoon emissions can be reduced by applying the waste in the spring instead of the fall to limit the time the lagoons are emitting. This would reduce emissions from lagoons 3 and 4 during the summer when emissions are the highest. This would also increase the N applied to the fields, and plant uptake would probably be enhanced because the grass is

not dormant as in the fall. Another advantage would be that a longer grazing period could be achieved. The aeration experiment demonstrated the value of testing. The aerators did not introduce enough oxygen into the lagoon to turn the lagoon aerobic. The cost of more powerful aerators to aerate the lagoon is probably prohibitive. A lower cost method is make the lagoons facultative lagoons by aerating the top layer of the lagoons with surface aerators. This would have three advantages: minimal NH_3 emissions since the concentration of NH_3 at the liquid surface is low, lower cost by only aerating only the surface layer of the lagoon, and most of the N in the lagoon is retained for fertilizer. Another method would be to cover the lagoon with a impermeable membrane but that would increase emissions from the slurry application unless another application method was used.

For waste application the best way to reduce emission would be to use a method where the slurry is applied directly to the field instead of using the "Big Gun". A trail hose method is probably the best choice since the soil is very hard and injecting the slurry would be difficult. This would put more N would in the soil and better coverage could be achieved. The disadvantages include increased labor costs and capital costs for new equipment.

The dairy farming industry needs information about what the NH_3 emissions are and how to reduce them. If funding is secured for future research, besides publishing in scientific journals, it would be helpful to the dairy industry to publish the results on the Internet where more people could have access to the information. An Internet based program that evaluates the N flow at a dairy and calculates NH_3 emissions based upon actual farm data would be helpful to the dairy industry to estimate emissions and evaluate the economics of different farming practices. A whole farm approach to NH_3 emission must be taken.

Chapter 10

Bibliography

American Public Health Association (APHA), 1992. *Standard Methods for the Examination of Water and Wastewater*, 18th ed. APHA, Washington, D.C..

Aneja, V.P., Chauhan, J.P., Walker, J.T., 2000. Characterization of atmospheric ammonia emissions from swine waste storage and treatment lagoons. *Journal of Geophysical Research*, 105 (D9), 11535-11545.

Aneja, V.P., Bunton, B., Walker, J.T., Malik, B.P., 2001a. Measurement and analysis of atmospheric ammonia emissions from anaerobic lagoons. *Atmospheric Environment*, 35, 1949-1958.

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

American Society of Agricultural Engineers, 1999. Design of anaerobic lagoons for animal waste management. ANSI/ASAE Standards EP403.3 Agricultural Engineering Yearbook. ASAE, St. Joseph, MI.

American Society of Agricultural Engineers, 2003. Manure production and characteristics. ASAE Standards D384.1 Agricultural Engineering Yearbook. ASAE, St. Joseph, MI.

Bouwman, A.F., Lee, D.S., Asman, W.A.H., Dentener, F.J., Van Der Hoek, K.W., Olivier, J.G.J., 1997. A global high-resolution emission inventory for ammonia. *Global Biogeochemical Cycles*, 11(4), 561-587.

Burgos, S.A., Robinson, P.H., Fadel, J.G., DePeters, E.J., 2005. Ammonia volatilization potential: prediction of urinary urea nitrogen output in lactating dairy cows. *Agriculture, Ecosystems and Environment*, 111, 261-269.

Busse, A.D., Zimmerman, J.R., 1973. User's guide for the Climatological Dispersion Model. U.S. Environmental Protection Agency Report R4-73-024.

Bussink, D.W. and Oenema, O., 1998. Ammonia volatilization from dairy farming systems in temperate areas: a review. *Nutrient Cycling in Agroecosystems*, 51, 19-33.

Campbell, G.S., Norman, J.M., 1998. *An Introduction to Environmental Biophysics*, Springer, New York.

Cassel, T., Ashbaugh, L., Flocchini, R., Meyer, D., 2005a. Ammonia flux from open-lot dairies: development of measurement methodology and emission factors. *Journal of the Air & Waste Management Association*, 55, 816-825.

Cassel, T., Ashbaugh, L., Flocchini, R., Meyer, D., 2005b. Ammonia emission factors for open-lot dairies: direct measurements and estimation by nitrogen intake. *Journal of the Air & Waste Management Association*, 55, 826-833.

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

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

De Visscher, A., Harper, L.A., Westerman, P.W., Lian, Z., Argo, J., Sharpe, R.R., Van Cleemput, O., 2002. Ammonia emissions from anaerobic swine lagoons: Model development. *Journal of Applied Meteorology*, 41, 426-433.

Dore, C.J., Jones, B.M.R., Scholtens, R., Huis in't Veld, J.W.H., Burgess, L.r., Phillips, V.r., Measuring ammonia emission rates from livestock buildings and manure stores-part 2: Comparative demonstrations of three methods on the farm. *Atmospheric Environment*, 38, 3017-3024.

Eklund, B., 1999. Comparison of line- and point-source releases of tracer gases. *Atmospheric Environment*, 33, 1065-1071.

Elzing, A., Monteny, G.J., 1997. Ammonia emission in a scale model of a dairy-cow house. *Transactions of the ASAE*, 40, 713-720.

EPA, 2004. National emissions inventory - ammonia emissions from animal husbandry operations draft report.

Ferm, M., Kasimir-Klemedtsson, A., Weslien, P., Klemedtsson, L., 1999. Emission of NH_3 and N_2O after spreading of pig slurry by broadcast or band spreading. *Soil Use and Management*, 15, 27-33.

Fernando, W.A.R.N., Xia, K., Rice, C.W., 2005. Sorption and desorption of ammonium from liquid swine waste in soils. *Soil Science Society of America Journal*, 69, 1057-1065.

Filipy, J., Rumburg, B., Mount, G., Westberg, H., Lamb, B., 2006. Identification and quantification of volatile organic compounds from a dairy. *Atmospheric Environment*, 40, 1480-1494.

Fuentes, J.P., Flury, M., Bezdicek, D.F., 2004. Hydraulic properties in a silt loam soil under natural prairie, conventional till and no-till. *Soil Science Society of America Journal*, 68, 1679-1688.

Fowler, D., Pitcairn, C.E.R., Sutton, M.A., Flechard, C., Laubet, B., Coyle, M., Munro, R.C., 1998. The mass budget of atmospheric ammonia in woodland within 1 km of livestock buildings. *Environmental Pollution*, 102(S1), 343-348.

Galle, B., Klemedtsson, L., Bergqvist, B., Ferm, M., Tornqvist, K., Griggith, D.W.T., Jensen, N., Hansen, F., 2000. Measurements of ammonia emissions from spreading of manure using gradient FTIR techniques. *Atmospheric Environment*, 34, 4907-4915.

Galloway, J.N., Schlesinger, W.H., Levy II, H., Michaels, A., Schnoor, J.L., 1995. Nitrogen fixation: anthropogenic enhancement-environmental response. *Global Biogeochemical Cycles*, 9(2), 235-252.

Galloway, J.N., 1998. The global nitrogen cycle: changes and consequences. *Environmental Pollution*, 102, 15-24.

Galloway, J.N., Cowling E.B., 2002. Reactive Nitrogen and the world: 200 years of change. *Ambio*, 31(2), 64-71.

Génermonet, S., Cellier, P., 1997. A mechanistic model for estimating ammonia volatilization from slurry applied to bare soil. *Agriculture and Forest Meteorology*, 88, 145-167.

Gilliland, A.B., Dennis, R.L., Roselle, S.J., Pierce, T.E., 2003. Seasonal NH₃ emission estimates for the eastern United States based on ammonium wet concentrations and an inverse modeling method. *Journal of Geophysical Research*, 108 (D15), doi:10.1029/2002JD003063.

Grady, C.P., Daigler, G. T., Lim, H.C., 1999. *Biological Wastewater Treatment*, 2nd ed. Marcel Dekker, New York.

Gray, N.F., 2004. *Biology of wastewater treatment*. 2nd Edition. Imperial College Press, London.

Harder, J.W., Jakoubek, R.O., Mount, G.H., 1997. Measurement of tropospheric trace gases by long-path differential absorption spectroscopy during the 1993 OH Photochemistry Experiment. *Journal of Geophysical Research*, 102 (D5), 6215-6226.

Harper, L.A., Sharpe, R.R., Parkin, T.B., 2000. Gaseous nitrogen emissions from anaerobic swine lagoons: Ammonia, nitrous oxide, and dinitrogen gas. *Journal of Environmental Quality*, 29, 1356-1365.

Howard, T., Lamb, B.K., Bamesberger, W.L., Zimmerman, P.R., 1992. Measurement of hydrocarbon emissions fluxes from refinery wastewater impoundments using atmospheric tracer techniques. *Journal of the Air & Waste Management Association*, 42, 1336-1344.

Hutchings, N.J., Sommer, S.G., Jarvis, S.C., 1996. A model of ammonia volatilization from a grazing livestock farm. *Atmospheric Environment*, 30 (4), 589-599.

- James, T., Meyer, D., Esparza, E., Depeters, E.J., Perez-Monti, H., 1999. Effects of dietary nitrogen manipulation on ammonia volatilization from manure for Holstein heifers. *Journal of Dairy Science*, 82, 2430-2439.
- Kamin, H., Barber, J.C., Brown, S.I., Delwiche, C.C., Grosjean, D., Hales, J.M., Knapp, J.L.W., Lemon, E.R., Martens, C.S., Niden, A.H., Wilson, R.P., Frazier, J.A.. 1979. *Ammonia*. University Park Press, Baltimore.
- Kaharabata, S.K., Schuepp, P.H., Desjardins, R.L., 2000. Estimating methane emissions from dairy cattle housed in a barn and feedlot using an atmospheric tracer. *Environmental Science and Technology*, 34, 3296-3302.
- Kohn, R.A., 2002. Nutrient Balancer Program. Maryland Cooperative Extension Verion 1.24.
- Koelliker, J.K., Miner, J.R., 1973. Desorption of ammonia from anaerobic lagoons. *Transactions of the ASAE*, 148-151.
- Lamb, B., Westberg, H., Allwine, G., 1986. Isoprene emission fluxes determined by an atmospheric tracer technique. *Atmospheric Environment*, 20 (1), 1-8.
- Lamb, B.K., McManus, J.B., Shorter, J.H., Kolb, C.E., Mosher, B., Harriss, R.C., Allwine, E., Blaha, D., Howard, T., Guenther, A., Lott, R.A., Siverson, R., Westberg, H., Zimmerman, P., 1995. Development of atmospheric methods to measure methane emissions from natural gas facilities and urban areas. *Environmental Science & Technology*, 29, 1468-1479.
- Langford, A.O., Fehsenfeld, F.C., 1992. natural vegetation as a source or sink for atmospheric ammonia: a case study. *Science*, 252, 581-583.
- Leneman, H., Oudendag, D.A., Van der Hoek, K.W., Janssen, P.H.M., 1998. Focus on emission factors: a sensitivity analysis of ammonia emission modelling in the Netherlands. *Environmental Pollution*, 102, 205-210.
- Ludwig, F.L., Liston, E.M., Salas, L.J., 1983. Tracer techniques fro estimating emissions from inaccessible ground level sources. *Atmospheric Environment*, 17 (11), 2167-2172.
- Mackenzie, F.T., 1998. *Our Changing Planet*, Second Edition. Prentice Hall, Upper Saddle River, 486pp.
- Malgeryd, J., 1998. Technical measures to reduce ammonia losses after spreading of animal manure. *Nutrient Cycling in Agroecosystems*, 51, 51-57.
- McCrorry, D.F. and P.J. Hobbs. 2001. Additives to reduce ammonia and odor emissions

from livestock wastes: a review. *Journal of Environmental Quality* 30:345-355.

Mellqvist, J., Rosen, A., 1996. DOAS for flue gas monitoring. II. Deviations from the Beer-Lambert law for UV-visible absorption spectra of NO, NO₂, SO₂, and NH₃. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 56, 209-224.

Methods for Chemical Analysis of Water and Wastes. March 1984. EPA-600/4-79-020. "Nitrogen, Ammonia" Method 350.1 (Colorimetric, Automated Phenate) Storet No. Total 00610, Dissolved 00608.

Middlebrooks, E.J., Middlebrooks, C.H., Reynolds, J.H., Watters, G.Z., Reed, S.C., George, D.B., 1982. Wastewater stabilization lagoon design, performance and upgrading. Macmillan, New York.

Misselbrook, T.H., Pain, B.F., Headon, D.M., 1998. Estimates of ammonia emission from dairy cow collecting yards. *Journal of Agricultural Engineering Research*, 71, 127-135.

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

Misselbrook, T.H., Webb, J., Chadwick, D.R., Ellis, S., Pain, B.F., 2001. Gaseous emissions from outdoor concrete yards used by livestock. *Atmospheric Environment*, 35, 5331-5338.

Misselbrook, T.H., Powell, J.M., Broderick, G.A., Grabber, J.H., 2005. Dietary manipulation in dairy cattle: laboratory experiments to assess the influence on ammonia emissions. *Journal of Dairy Science*, 88, 1765-1777.

Monteny, G.J., Schulte, D.D., Elzing, A., Lamaker, E.J.J., 1996. Prediction modelling of ammonia emissions from cubicle dairy cow houses. *Proceedings of the 1st International Conference on Air Pollution from Agricultural Operations*. Kansas City, Missouri, USA, 1996, 215-220.

Monteny, G.J., Schulte, D.D., Elzing, A., Lamaker, E.J.J., 1998. A conceptual mechanistic model for the ammonia emissions from free stall cubicle dairy cow houses. *Transactions of the ASAE*, 41, 193-201.

Mount, G.H., Rumburg, B., Havig, J., Lamb, B., Westberg, H., Yonge, D., Johnson, K., Kinciad, R., 2002. Measurement of atmospheric ammonia at a dairy using differential optical absorption spectroscopy in the mid-ultraviolet. *Atmospheric Environment*, 36, 1799-1810.

Nash, J.C., 1990. *Compact Numerical Methods for Computers, Linear Algebra and Function Minimization*. Adam Hilger, New York.

National Research Council, 2001. *Nutrient requirements of dairy cattle*, 7th revised edi-

tion. Washington, D.C.: National Academic Press.

National Research Council. 2003. Air Emissions from Animal Feeding Operations: Current Knowledge, Future Needs. Washington, D.C.: National Academic Press.

Natural Aeration Inc.. <http://www.circul8.com>.

Neger, M.K. (2002) Monitoring and evaluation of an anaerobic dairy lagoon. Masters thesis, Washington State University.

Nennich, T.D., Harrison, J.H., VanWieringen, Meyer, D., Heinrichs, A.J., Weiss, W.P., St-Pierre, N.R., Kincaid, R.L., Davidson, D.L., Block, E., 2005. Prediction of manure and nutrient excretion from dairy cattle. *Journal of Dairy Science*, 88, 3721-3733.

Ni, J., 1999. Mechanistic models of ammonia release from liquid manure: a review. *Journal of Agricultural Engineering Resources*, 72, 1-17.

Nommik, H, Vahtras, K., 1982. Retention and fixation of ammonia and ammonium in soils. In: Stevenson, J. (Ed.) *Nitrogen in Agricultural Soils*. Agronomy Monograph no. 22, 123-171.

National Research Council, 2003. Air Emissions from Animal Feeding Operations: Current Knowledge, Future Needs. National Academic Press, Washington, D.C..

NZAEI, 1984. *Agricultural Waste Manual*. NZAEI Project Report No. 32. December 1984. Lincoln College, Canterbury, New Zealand: Agriculture Engineering Institute.

Oswald, W.J., 1968. Advances in anaerobic pond systems design. In: Gloyna, E.F., Eckenfelder, W.W., (Eds.), *Advances in water quality improvement*. University of Texas Press, Austin.

Pain, B.F., Thompson, R.B., Rees, Y.J., Skinner, J.H., 1990. Reducing gaseous losses of nitrogen from cattle slurry applied to grassland by the use of additives. *Journal of the Science of Food and Agriculture*, 50, 141-153.

Pinder, R.W., Penkney, N.J., Davidson, C.I., Adams, P.J., 2004. A process-based model of ammonia emissions from dairy cows; improved temporal and spatial resolution. *Atmospheric Environment*, 38, 1357-1365.

Pinder, R.W., Strader, R., Davidson, C.I., Adams, P.J., 2004. A temporally and spatially resolved ammonia emission inventory for dairy cows in the United States. *Atmospheric Environment*, 3747-3756.

Pollet, I., Christiaens, J., Van Langenhove, H.V., 1998. Determination of the ammonia emissions from cubicle houses for dairy cows based upon a mass balance. *Journal of Agri-*

cultural Engineering Resources, 71, 239-248.

Rumburg, B., Neger, M., Mount, G.H., Yonge, D., Filipy, J., Swain, J., Kincaid, R., Johnson, K. 2004. Liquid and atmospheric ammonia concentrations from a dairy lagoon during an aeration experiment. *Atmospheric Environment*, 38, 1523-1533.

Rumburg, B., Mount, G.H., Yonge, D., Lamb, B., Westber, H., Filipy, J., Bays, J., Kincaid, R., Johnson, K. Atmospheric Flux of Ammonia from Sprinkler Application of Dairy Waste. submitted to *Atmospheric Environment* 2005.

Schwartz, J., 1994. Air pollution and daily mortality: a review and meta analysis. *Environmental Research*, 64, 36-52.

Seinfeld, J.H., Pandis, S.N., 1996. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. John Wiley & Sons, Inc., New York, 1326pp.

Sharpe, R.R., Harper, L.A., 1997. Ammonia and nitrous oxide emissions from sprinkler irrigation applications of swine effluent. *Journal of Environmental Quality*, 26, 1703-1706.

Shorter, J.H., McManus, J.B., Kolb, C.E., Allwine, E.J., Siverson, R., Lamb, B.K., Mosher, B.W., Harriss, R.C., Howard, T., Lott, R.A., 1997. Collection of leakage statistics in the natural gas system by tracer methods. *Environmental Science & Technology*, 31, 2012-2019.

Simunek, J., van Genuchten, M.T., Sejna, M., 2005. *The HYDRUS-1D Software Package for Simulating the Movement of Water, Heat, and Multiple Solutes in Variably Saturated Media, Version 3.0, HYDRUS Software Series 1*, Department of Environmental Sciences, University of California Riverside, Riverside, California, USA, 270 pp.

Sneath, R.W., Burton, C.H., Williams, A.G., 1992. Continuous aerobic treatment of piggery slurry for odour control scaled up to a farm-size unit. *Journal of Agricultural Engineering Research*, 53, 81-92.

Snoeyink, V.L., Jenkins, D., 1980. *Water Chemistry*. John Wiley & Sons, USA.

Søgaard, H.T., Sommer, S.G., Hutchings, N.J., Huijsmans, J.F.M., Bussink, D.W., Nicholson, F., 2002. Ammonia volatilization from field-applied animal slurry-the ALFAM model. *Atmospheric Environment*, 36, 3309-3319.

Sommer, S.G., Olesen, J.E., 1991. Effects of dry matter content and temperature on ammonia loss from surface-applied cattle slurry. *Journal of Environmental Quality*, 20, 679-683.

Sommer, S.G., Christensen, B.T., Nielsen, N.E., Schjorring, J.K., 1993. Ammonia volatilization during storage of cattle and pig slurry: effect of surface cover. *Journal of Agricultural Science*, 121, 63-71.

Sommer, S.G., 1997. Ammonia volatilization from farm tanks containing anaerobically di-

gested animal slurry. *Atmospheric Environment*, 31, 863-868.

Sommer, S.G., Friis, E., Bach, A., Schjorring, J.K., 1997. Ammonia volatilization from pig slurry applied with trail hoses or broadcast to winter wheat: Effects of crop development stage, microclimate, and leaf ammonia absorption. *Journal of Environmental Quality*, 20, 679-683.

Sommer, S.G., Olesen, J.E., 2000. Modelling ammonia volatilization from animal slurry applied with trail hoses to cereals. *Atmospheric Environment*, 34, 2361-2372.

Sommer, S.G., Hansen, M.N., Sogaard, H.T., 2004. Infiltration of slurry and ammonia volatilisation. *Biosystem Engineering*, 88 (3), 359-367.

Sund J.L., C.J. Evenson, K.A. Strevett, R.W. Nairn, D.Athay, and E. Trawinski. 2001. Nutrient conversions by photosynthetic bacteria in a concentrated animal feeding operation lagoon system. *Journal of Environmental Quality* 30:648-655.

Suto, M., Lee, L.C., 1983. Photodissociation of NH_3 at 106-200 nm. *Journal of Chemical Physics*, 78, 4515.

Sutton, M.A., Milford, C., Dragosits, U., Place, C.J., Singles, R.J., Smith, R.I., Pitcairn, C.E.R., Fowler, D., Hill, J., ApSimon, H.M., Ross, C., Hill, R., Jarvis, S.C., Pain, B.F., Phillips, V.C., Harrison, R., Moss, D., Webb, J., Espenhahn, S.E., Lee, D.S., Hornung, M., Ullyett, J., Bull, K.R., emmett, B.A., Lowe, J., Wyers, G.P., 1998. Dispersion, deposition and impacts of atmospheric ammonia: quantifying local budgets and spacial variability. *Environmental Pollution*, 102 (S1), 349-261.

Sweeten, J.M., Wolfe, M.L., 1994. Manure and wastewater management systems for open lot dairy operations. *Transactions of the ASAE*, 37(4), 1145-1154.

Thompson, R.B., Meisinger, J.J., 2004. Gaseous nitrogen losses of ammonia volatilization measurement following land application of cattle slurry in the mid-Atlantic region of the USA. *Plant and Soil*, 266, 231-246.

Turner, D.B., 1970. Workbook of atmospheric dispersion estimates. U.S. Public Health Service Publication 999-AP-26.

United States Department of Agriculture Animal and Plant Health Inspection Service, Waste Handling Facilities and Manure Management on U.S. Dairy Operations: http://www.aphis.usda.gov/vs/ceah/cahm/Dairy_Cattle/d96wast.htm.

US Department of Agriculture Animal and Plant Health Inspection Service, Waste Handling Facilities and Manure Management on U.S. Dairy Operations: <http://www.aphis.usda.gov/vs/ceah/ncahs/nahms/dairy/index.htm>

- van Aardenne, J.A., Dentener, F.J., Olivier, G.J., Klein Goldewijk, C.G.M., Lelieveld, J., 2001. A 1° x 1° resolution data set of historical anthropogenic trace gas emissions for the period 1890-1990. *Global Biogeochemical Cycles*, 15(4), 909-928.
- Van Breemen, N., Burrough, P.A., Velthorst, E.J., Van Dobben, H.F., de Wilt, T., Ridder, T.B., Reijnders, H.F.R., 1982. Soil acidification from ammonium sulfate in forest canopy throughfall. *Nature*, 299, 548-550.
- Vitousek, P.M., Aber, J.D., Howarth, G.E., Likens, G.E., Watson, P.A., Schindler, D.W., Schlesinger, W.H., Tilman, D.W., 1997. Human alterations of the global nitrogen cycle: sources and consequences. *Ecological Applications*, 7, 737-750.
- Warneck, P., 1988. *Chemistry of the Natural Atmosphere*. Academic Press, New York.
- Westerman, P.W., Zhang, R.H., 1997. Aeration of livestock manure slurry and lagoon liquid for odor control: a review. *Applied Engineering in Agriculture*, 13, 245-249.
- Wetherelt, S.H., 2003. Determination of the nitrogen budget for the Washington State University Knott Dairy Center. Masters Thesis.
- Wu, J., Nofziger, D.L., Warren, J.G., Hattey, J.A., 2003. Modeling ammonia volatilization from surface-applied swine effluent. *Soil Science Society of America Journal*, 67, (1), 1-11.
- Wulf, S., Maeting, M., Clemens, J., 2002a. Application technique and slurry cofermentation effects on ammonia, nitrous oxide, and methane emissions after spreading: I. ammonia volatilization. *Journal of Environmental Quality*, 31, 1789-1794.
- Wulf, S., Maeting, M., Clemens, J., 2002b. Application technique and slurry cofermentation effects on ammonia, nitrous oxide, and methane emissions after spreading: II. greenhouse gas emissions. *Journal of Environmental Quality*, 31, 1795-1801.
- Yang, Z., Niimi, H., Kanda, K., Suga, Y., 2003. Measurement of ammonia volatilization from a field, in upland Japan, spread with cattle slurry. *Environmental Pollution*, 121, 463-467.