The Effects of Manure Handling and Dietary Protein on Ammonia Emissions from a Flush Dairy

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ABSTRACT

Atmospheric ammonia ($NH_{3(g)}$) poses an environmental concern mainly due its ability to form fine particulate matter ($PM_{2.5}$ with a diameter smaller than 2.5 μm) in the form of ammonium nitrate (NH_4NO_3) and ammonium sulfate ($[NH_4]_2SO_4$). These forms of $PM_{2.5}$ may reduce visibility, contribute to eutrophication through deposition, and be detrimental to human health through inhalation. A more complete understanding of ammonia emissions may bring significant $PM_{2.5}$ reductions within grasp.

According to recent studies, one of the largest contributors to atmospheric ammonia is dairy cattle excreta. In this study, seven lactating Holstein cows were subjected to four feeding trials with diets containing 14.5, 15.5, 17, and 18% crude protein (CP). The first objective was to determine the effect of protein content/intake on ammonia fluxes to the atmosphere from each stage of manure handling at a flush dairy. The second objective was to examine the effect of manure handling itself on ammonia fluxes. We examined four different stages of manure handling:

1. Fresh mixture of urine and feces to represent what may be *scraped* from a barn floor
2. Diluted mixture of urine and feces to represent what is *flushed* from a barn floor
3. Solids portion of a diluted mixture of urine and feces to represent what is *retained* by a solids separator at a dairy
4. Liquid portion of a diluted mixture of urine and feces to represent the *permeate* from a solids separator at a dairy

Ammonia fluxes from scraped manure began low and rose to higher fluxes and peaked at an average of 25 hours after mixing urine and feces. Fluxes from flushed manure showed the same behavior. The average pH values for the scraped and flushed manure were relatively low at 6.87±0.17 and 7.05±0.13, respectively, and unfavorable toward ammonia versus ammonium. Fluxes from the separated solids and liquid manure, whose pH values were higher at 8.70±0.30 and 8.55±0.19, respectively, peaked almost immediately. For a time period of 18 hours after beginning flux measurements from the separated liquid manure, fluxes stayed relatively constant. Compared to hours 0-9, fluxes from the separated solids manure decreased 11% in hours 9-18.

These results indicate that ammonia fluxes from the scraped and flushed manure were initially limited by the relatively low pH of the slurries, until they aged and released carbon dioxide, after which fluxes became controlled by temperature. Fluxes from the separated solids and liquid manure, however, were temperature-controlled from the start, as this manure had already undergone some aging and the initial pH was more favorable to ammonia loss.

Multivariable regressions predicting the mass of ammonia lost to the atmosphere as a function of total ammoniacal nitrogen (TAN) and temperature (T) show that fluxes from the scraped and flushed manure are very sensitive to temperature compared to the separated solids and liquid manure. The same regressions show that ammonia fluxes from the separated solids and liquid manure are predicted well by TAN and T (R^2 = 0.906 and 0.812, respectively), indicating that dietary protein manipulation, which affects TAN content of the manure, may have a greater effect in this stage of handling. Regressions predicting the mass of ammonia lost to the atmosphere as a function of crude protein intake show crude protein intake is a poor predictor of the overall ammonia flux from a flush dairy. Low correlation coefficients from these regressions are likely a result of cow-to-cow variability in the effect of crude protein intake on ammonia emissions.

Significant reductions in ammonia fluxes are possible; however, they will require new regulations on manure handling at flush dairies or incentives for flush dairies to pursue alternate means of manure handling with low emissions. Dairies can begin attacking the problem of excessive emissions by lowering the dietary protein content for older cows to reduce the mass of TAN excreted in their manure, thereby reducing ammonia fluxes in accordance with Henry's law. Once manure is excreted on the barn floor, dairies must encourage mixing between urine and feces and use the natural acidity of the feces in delaying emissions by converting aqueous ammonia in the urine to ammonium. Dairies can achieve well-mixed slurries by manually mixing the manure or with a sloped floor, channeling urine and feces to a common area. Covering holding tanks containing flushed manure to minimize CO_2 stripping and a rise in pH is one measure that may reduce ammonia fluxes. Finally, requiring nitrification or nitrification and denitrification in on-site storage tanks will biologically convert ammonia to nitrate or nitrogen gas, respectively, reducing fluxes from the separated liquid manure. Although burdensome to dairies, these measures would drastically reduce ammonia emissions from flush dairies. Regulatory agencies may choose to ignore the separated solids manure when considering

strategies to reduce ammonia emissions, since ammonia volatilization becomes limited by aqueous ammonia in the first 18 hours following separation.

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Prof. Linsey Marr- Ph.D. (Department of Environmental Engineering) is the primary advisor and committee chair. Dr. Marr provided her technical expertise during the construction of the materials used in this project and during data collection. Dr. Marr was also responsible for validating results, suggesting methods of data presentation in this thesis, and improving the writing style. Additionally, she contributed to the proposal.

Linsey Marr received her B.S. from Harvard College in Engineering Science in 1996 and her Ph.D. from UC, Berkeley in Environmental Engineering in 2002. Dr. Marr started her professorship with Virginia Tech in 2003. She has received multiple awards and honors during her career as a professor thus far, including the NSF Career Award. Dr. Marr's areas of expertise include nanoparticle emissions, motor vehicle emissions, air quality modeling, and polycyclic aromatic hydrocarbons (PAH) emissions and exposure.

I would like to give out a special thanks to Linsey. Without her motivation and support, I would not have been able to complete this thesis.

Prof. Jactone Arogo Ogejo- Ph.D. (Department of Biological Systems Engineering) provided his expertise on agricultural waste and ammonia emissions from agricultural operations. Dr. Jactone Arogo Ogejo was the first to suggest that pH may be the controlling factor in the slow rise in fluxes from the scraped and flushed manure.

Dr. Jactone Arogo Ogejo earned a B.S. from the University of Nairobi, Kenya in Agricultural Engineering in 1983, a M.S. from the University of Illinois, Urbana-Champaign in Agricultural Engineering in 1989, and a Ph.D. from the University of Illinois, Urbana-Champaign in Agricultural Engineering in 1997. His areas of expertise include energy and nutrient recovery from biobased materials, animal waste management, and agricultural air quality.

Prof. Mark Hanigan- Ph.D. (Department of Dairy Science) advised the graduate students responsible for cow health, housing, and manure collection. Additionally, Dr. Hanigan approved feeding schedules and supervised students occasionally involved in dairy operations. He was also involved in the proposal.

Mark Hanigan received a B.S. from Iowa State University in Dairy Science in 1987, a M.S. from UC, Davis in Animal Science in 1989, and a Ph.D. from UC, Davis in Nutrition in 1991, with a minor in Physiological Chemistry. Dr. Hanigan began his professorship with Virginia Tech in 2005. Prior to becoming a professor and even before his academic training, he owned a dairy farm in Denison, Iowa (1979-1983) and worked as a research scientist for Land O' Lakes/Purina Feed. Dr. Hanigan is a member of the American Dairy Science Association, the American Society of Animal Science, and the American Society for Nutrition. His areas of expertise include animal nutrition, nutrient metabolism, and metabolic modeling.

Prof. Katharine Knowlton- Ph.D. (Department of Dairy Science) also advised graduate students responsible for cow health, housing, and manure collection. She supervised laboratory technicians responsible for analyzing sub-samples of manure for TAN and TKN. Dr. Knowlton also contributed to the proposal.

Dr. Knowlton earned a B.S. from Cornell University in Animal Science in 1991, a M.S. from Michigan State University in Dairy Nutrition in 1993, and a Ph.D. from the University of Maryland & USDA-ARS Beltsville in Dairy Nutrition in 1997. Dr. Knowlton began her professorship with Virginia Tech in 2000. In addition to her academic training, Dr. Knowlton also has experience as a farm manager from her time at a dairy farm in Portland, CT (1984-1987). She has received a number of awards in her field including the American Dairy Science Association Scholar Award in Dairy Production. Her areas of expertise include environmental issues associated with agriculture and ruminant phosphorus digestion and metabolism.

Prof. Susan Gay- Ph.D. (Department of Biological Systems Engineering) aided in the proposal and project startup. Dr. Gay earned a B.S. from Cornell University in 1992, a M.S. from Pennsylvania State University in 1996, and a Ph.D. from Pennsylvania State University in 2000. Her areas of expertise include environmental effects of poultry and livestock operations, gaseous emissions from agricultural operations, and air quality monitoring.

Joby Cyriac (Department of Dairy Science) is a Ph.D. student working under Dr. Hanigan. Joby aided in manure collection, provided data for feed weights, and determined the TAN and TKN for both urine and feces collected during each sampling period. Joby also maintained cow housing and monitored cow health. Joby earned a B.Vsc. in India and a M.S. from South Dakota State University.

Karen Hall (Department of Dairy Science) is a laboratory technician working under Dr. Knowlton. Karen determined the TAN and TKN of manure slurries prior to and following ammonia gas measurements. Karen earned a M.S. from Virginia Tech.

Sarah Slagle (Department of Environmental Engineering) is a laboratory technician who worked under Dr. Marr. Sarah constructed the flux chambers, determined background ammonia concentrations at the dairy, obtained preliminary results in validating the flux chambers, and contributed to the literature review. Sarah earned a B.S. from Virginia Tech.

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1 Introduction

Mainly due to its ability to form fine particulate matter, defined as particles with diameters smaller than 2.5 μm ($PM_{2.5}$), atmospheric ammonia has the potential to be detrimental to human health, the economy, and the environment. To reduce $PM_{2.5}$, the sources of its precursors must be identified. In the eastern US, the majority of $PM_{2.5}$ is composed of ammonium nitrate (NH_4NO_3) and ammonium sulfate ($[NH_4]_2SO_4$). Both compounds form via heterogeneous reactions involving precursor gases: sulfur dioxide (SO_2), nitric oxides (NO_x), and ammonia (NH_3). SO_2 and NO_x have been studied extensively, resulting in an abundance of technologies that are capable of achieving emissions reductions for these compounds [1]. However, there still exist areas of the US where ammonia is the limiting factor in $PM_{2.5}$ formation [2]. Yet, efforts to reduce ammonia emissions are still lacking. Only in the past decade have researchers uncovered the sources of atmospheric ammonia, which include livestock manure, soils and vegetation, fertilizer application, industrial sources, and motor vehicles [1].

In an effort to improve ammonia emissions inventories developed in the mid-1990s, Battye et al. [1] performed studies in Charlotte, NC and Fresno, CA to determine sources of atmospheric ammonia and their respective contributions. They found that animal production was the largest contributor to ammonia emissions in the study areas, amounting to 80 and 64% in Charlotte and Fresno, respectively.

Livestock manure, specifically dairy cow manure, is the focus of this thesis research because it has been found to be one of the largest sources of ammonia emissions to the atmosphere. Misselbrook et al. [3] compiled results from publications pertaining to agricultural sources of ammonia in the United Kingdom and showed that, on a per animal basis, dairy cattle contribute more ammonia to the atmosphere than all other grazing domesticated animals at 16.9 grams of ammonia as nitrogen per animal per day (g N $animal^{-1}$ d^{-1}). Ultimately, Misselbrook et al. [3] were able to conclude that the broader subcategory of all cattle, including dairy, is responsible for approximately 50% of the agricultural ammonia emitted each year. This conclusion was based on ammonia lost from animal housing, manure storage and handling, and grazing.

Bouwman et al. [4] also developed estimates of ammonia emissions from agricultural sources but over a global scale. The study [4] found that dairy cattle emit approximately 2.1 Tg N yr^{-1} (5.8×10^6 g N d^{-1}), only exceeded by nondairy cattle, which contribute approximately 2.2 Tg N yr^{-1} (6.0×10^6 g N d^{-1}). Emissions from swine were third highest in magnitude at 1.4 Tg N yr^{-1} (3.8×10^6 g N d^{-1}). Concurring with Misselbrook et al. [3], Bouwman et al. [4] found that cattle account for more than 50% of the agricultural ammonia emitted each year.

1.1 Research Objectives

The overall objective of the research is to quantify the potential of dietary protein manipulation and manure handling optimization to reduce emissions of ammonia from manure in dairy housing and manure storage facilities.

This thesis research involved two separate studies. In the first study, we tested the effect of manure handling techniques and dietary protein manipulation on ammonia emissions from dairy manure exposed to ambient temperature fluctuations. The second study had the same objectives, but we moderately controlled the temperature of the manure.

The first research objective was to determine how ammonia emissions from dairy manure varied during each stage of manure of handling by a dairy utilizing a flush system. The four stages of handling are listed below.

1. Fresh mixture of urine and feces to represent what may be *scraped* from a barn floor
2. Diluted mixture of urine and feces to represent what is *flushed* from a barn floor
3. Separated Solids – What was *retained* in a solids separator following separation of a diluted mixture of urine and feces
4. Separated Liquid – *Permeate* from a solids separator following separation of a diluted mixture of urine and feces

The second research objective was to test the effect of dietary protein on ammonia emissions from dairy manure. We fed Holstein cows four diets formulated to contain 14.5, 15.5, 17, and 18.0% crude protein (CP). We used a dynamic flux chamber to measure fluxes of ammonia from their manure under the different types of manure handling.

1.2 Effects of Atmospheric Ammonia

$PM_{2.5}$ is defined as particulate matter whose aerodynamic diameter is less than 2.5 μm. In contrast with coarse particulate matter (PM_{10} or larger), which can only penetrate as far as the bronchial region of the lungs upon inhalation, $PM_{2.5}$ is able to penetrate deep into the alveolar region. Therefore, it is considered to be a greater health hazard. One study [2] showed that exposure to fine particulate matter is associated with premature mortality, chronic bronchitis, and asthma attacks. Pope et al. [5] surveyed approximately 319,000 adults across 51 metropolitan areas in the US. The study compiled $PM_{2.5}$ exposure data from 1979 to 1983 and from 1999 to 2000, as well as death certificates containing cause of death for those participants who were deceased following the exposure periods. Results showed strong correlations between $PM_{2.5}$ exposure and cardiopulmonary and lung cancer mortality. Pope et al. [5] concluded that a 10 $\mu g\ m^{-3}$ rise in mean ambient $PM_{2.5}$ concentration corresponded to a 4, 6, and 8% increase in the risk of all-cause, cardiopulmonary, and lung cancer mortality, respectively. Correlations between fluctuations in coarse particulate matter concentrations and mortality were not significant.

Economic Effects

Pope et al.'s study [5] suggests that increased exposure to fine particulate matter would cause increased healthcare spending. McCubbin et al. [2] determined the economic benefits of reducing ammonia emissions in the US alone. The study estimated the average value of a statistical life to be $5.6 million and listed low and high monetary values associated with mortality reductions to account for the uncertainty in reducing emissions (Table 1.1). The largest savings resulted from emission reductions from confined cattle operations using diet optimization as a control scenario, an outcome that provides the motivation for this thesis research.

Table 1.1: Ammonia emission reductions and corresponding monetary values (adapted from McCubbin et al. [2])

Control Scenario	Interval Boundaries	Emission Reduction (%)	Mortality Reduction	Monetary Value (millions 1999 $[a])
Diet Optimization	Low	4.7	232	1,298
	High	15.6	790	4,423
Emissions Reduction[b]	-	10	498	2,787
	-	20	1,024	5,732

[a]Monetary value in 1999 dollars saved over a 5-yr period
[b]Overall emission reductions from confined cattle operations using various control scenarios such as diet optimization, chemical treatment of cattle manure, manure storage management, and land incorporation of cattle manure

The other control scenarios, such as urease inhibition, storage management, and land incorporation, provided for lower emission reductions than those corresponding to diet optimization. It should also be noted that if overall emission reductions are kept constant, mortality reductions and monetary values will be greater from confined cattle operations than from other confined animal feeding operations (CAFOs). This is due to the greater atmospheric ammonia contribution from cattle than from other agricultural sources.

Environmental Effects

Wet deposition of atmospheric ammonia has contributed to eutrophication in estuaries, such as the Chesapeake Bay, especially in regions where phytoplankton are nitrogen limited. A study performed by Russell et al. [6] found a volume weighted average ammonium (NH_4^+) concentration of 13.6 μmol L^{-1} (0.245 mg L^{-1}) in precipitation entering the Chesapeake Bay. Through a combination of stable nitrogen isotope data and obvious seasonal patterns of ammonium concentrations in the precipitation, the researchers were able to pinpoint the ammonia emission sources responsible for the ammonium in wet deposition. The study concluded that the majority of ammonium originated from agricultural operations.

A study performed by VanderEerden et al. [7] found an ammonium concentration between 40 and 62 μmol L^{-1} (0.72 mg L^{-1} and 1.1 mg L^{-1}, respectively) in precipitation in the Netherlands, values much higher than those reported by Russell et al. [6]. This result is not surprising since the Netherlands has the highest nitrogen deposition in Europe. Just as Russell et al. [6] examined the detrimental effects of nitrogen deposition in water, VanderEerden et al. [7] studied the effects on land. Already aware that deposition may cause plant stress from nutrient

overload, acidic soil conditions as a result of nitrification, and/or flourishing of invasive nitrophilous plant species, VanderEerden et al. [7] searched for possible evidence of detrimental effects on Dutch forests. Results showed dramatic reductions in tree vitality, foliage discoloration, and reductions in non-nitrophilous plant species by as much as 12%. Nitrogen deposition was noted as a potential contributing factor to but not necessarily the sole cause of these phenomena.

Ammonia has the ability to promote climate change based on its ability to form $PM_{2.5}$, specifically ammonium sulfate particles [8]. This form of particulate matter can possibly increase the earth's albedo in two ways. Particles can either backscatter UV and visible radiation directly, reducing the amount that reaches the earth's surface, or indirectly by increasing cloud cover due to increased numbers of cloud condensation nuclei, particles that give rise to cloud formation.

1.3 Gaseous Ammonia Formation from Cattle Manure

This research focuses on ammonia emissions from cattle urine and feces mixtures, or slurries. Urease is the enzyme in bovine feces that plays an important role in promoting ammonia emissions from a slurry. It is responsible for the hydrolysis of urea in the urine, which yields ammonium, bicarbonate, and hydroxyl ions (Equation 1.1) [4].

$$CO(NH_2) + 3H_2O \xrightarrow{\text{Urease}} 2NH_4^+ + HCO_3^- + OH^-$$

Equation 1.1: Urea hydrolysis

On average, only 3% of nitrogen in cow urine is present as ammonia-nitrogen following excretion, while approximately 70% exists as urea [9]. The other 27% consists of allantoin, hippuric acid, creatinine, creatine, and uric acid. Due to such high urea content, urease availability and activity will play a key role in ammonia-nitrogen formation. Urease activity is dependent on slurry pH, temperature, and urea concentration of the urine. As with most chemical and biological processes, urease activity increases with temperature between 10 and 40^{o}C and reaches a maximum near a neutral pH (between 6.8 and 7.6) [10].

Muck [10] describes urea hydrolysis using Michaelis-Menten kinetics, which seems appropriate since they are typically used to describe enzyme activity (Equation 1.2). However, Sherlock and Goh [11] have shown Michaelis-Menten kinetics to poorly describe urea

hydrolysis, and that it is better described by first-order kinetics (Equation 1.3). The effect of urea concentration on urease activity is obvious. A reduction in initial urea concentration corresponds to a directly proportional reduction in urea concentration at time t.

$$V = \frac{(C_0 - C)}{t}$$

Equation 1.2: Urease activity as defined by Michaelis-Menten kinetics [10]

$$C = C_0 \times e^{(-kt)}$$

Equation 1.3: Urease activity as defined by first-order kinetics [11]

Where: C = urea concentration at time t, mg N $(L\ slurry)^{-1}$
C_0 = urea concentration at time t_0, mg N $(L\ slurry)^{-1}$
k = first-order hydrolysis constant, d^{-1}
t = time, d
V = urease activity, mg N $(L\ slurry)^{-1}\ d^{-1}$

Urea hydrolysis by urease only describes the formation of the ammonium ion, the first step in gaseous ammonia production. The second step is described by the acid/base equilibrium between the ammonium ion and aqueous ammonia (Equation 1.4).

$$NH_4^+ \leftrightarrow NH_3 + H^+$$

Equation 1.4: Dissociation of the ammonium ion in solution

This equilibrium is also affected by temperature and pH. Low temperature slows the dissociation of the ammonium ion, while a high temperature favors it [12]. Following Le Chatelier's Principle, an increase in pH results in increased aqueous ammonia and a decrease in pH yields increased ammonium. The pK_a for this equilibrium is 9.25 at a temperature of 25°C.

Ammonia Mass Transfer

The mass transfer of ammonia from the aqueous phase to the gaseous phase describes the third and last step in gaseous ammonia production. Equilibrium partitioning for dilute solutions (< 1000 mg $NH_{3(aq)}\ L^{-1}$) can be quantified by Henry's constant (K_H) [13]. For ammonia, Henry's law states that the gaseous ammonia concentration ($C_{NH3(g)}$) above a dilute solution (< 1000 mg

$NH_{3(aq)}$ L^{-1}) is directly proportional to the aqueous ammonia concentration ($C_{NH3(aq)}$) (Equation 1.5). There have been at least 12 authors that have attempted to use Henry's law to model the mass transfer of ammonia from the aqueous to the gaseous phase in agricultural scenarios [14]. These models, which typically use K_H as a predictor variable, define K_H in terms of temperature (Equation 1.6, Equation 1.7, Equation 1.8, and Equation 1.9).

$$K_H = \frac{C_{NH_{3(g)}}}{C_{NH_{3(aq)}}}$$

Equation 1.5: Henry's law for ammonia [14]

Where: K_H = Henry's constant
$C_{NH_{3(g)}}$ = gas-phase ammonia concentration
$C_{NH_{3(aq)}}$ = aqueous-phase ammonia concentration

K_H is highly sensitive to temperature (T), and the van't Hoff equation describes this relationship for a multitude of gases [8]. Equation 1.6 shows the van't Hoff equation with constants for ammonia.

$$K_{H-2} = K_{H-1} \times e^{\left[{}^{\Delta H}/_{R}\left({}^{1}/_{T_1} - {}^{1}/_{T_2}\right)\right]}$$

Equation 1.6: van't Hoff equation [8]

Where: K_{H-2} = Henry's constant at T_2
T_2 = temperature, K
K_{H-1} = Henry's constant at T_1
T_1 = temperature, K
ΔH = enthalpy of solution for ammonia, -8.17 kcal mol^{-1}
R = ideal gas constant, 0.001987 kcal K^{-1} mol^{-1}

Wu et al. [15] presents a relationship between K_H and T as it pertains to ammonia emissions from land-applied swine manure (Equation 1.7).

$$K_H = \frac{e^{\left(158.17 - {}^{8621}/_{T} - 25.677\ln(T) + 0.0354T\right)}}{RT}$$

Equation 1.7: Henry's constant for ammonia as a function of temperature as defined by Wu et al. [15]

Where: T = temperature, K
R = ideal gas constant, 0.008315 kJ K^{-1} mol^{-1}

Sherlock and Goh [11] and Monteny et al. [16] present relationships between K_H and T pertaining to ammonia emissions from cattle manure (Equation 1.8 and Equation 1.9).

$$K_H = \frac{1}{10^{(-1.69 + 1477.7/T)}}$$

Equation 1.8: Henry's constant for ammonia as a function of temperature as defined by Sherlock and Goh [11]

$$K_H = \frac{1}{1384 \times 1.053^{(293-T)}}$$

Equation 1.9: Henry's constant for ammonia as a function of temperature as defined by Monteny et al. [16]

The van't Hoff equation and the three relationships between K_H and T from the literature show similar behaviors and similar values for K_H at equal temperatures. However, the relationship developed by Monteny et al. [16] shows a higher rate of change in K_H as T increases, providing for higher values for K_H at higher temperatures (Figure 1.1).

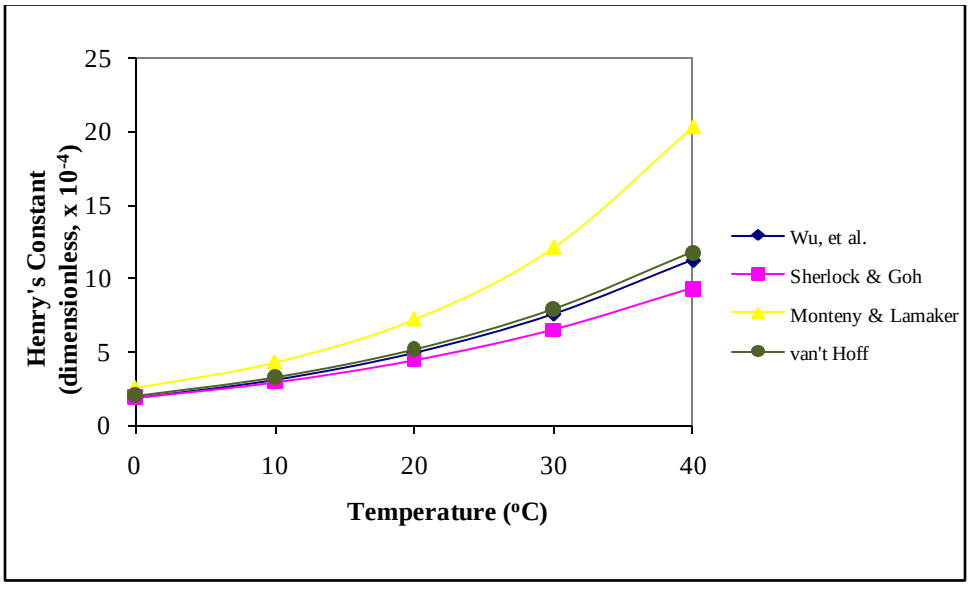

Figure 1.1: Effect of temperature on Henry's constant as determined by the van't Hoff equation and three studies

These relationships become important to this thesis research in the analysis and temperature correction of results.

Slurry pH

Temperature and pH have effects on all three steps in gaseous ammonia evolution from manure. Temperature fluctuations in manure are typically caused by ambient temperature fluctuations and, therefore, follow a diurnal pattern. This is due to the fact that cattle manure is typically excreted in a pasture, in a feeding lot, or on a barn floor, and most CAFOs do not provide temperature control. pH fluctuations are more complicated. If manure is acidic, the total ammoniacal nitrogen (TAN) will remain as ammonium (produced from urea hydrolysis) due to the ammonium/ammonia acid/base equilibrium. Under these conditions, the loss of carbon dioxide from manure to the atmosphere will result in an increase in pH [17]. As the pH and concentration of aqueous ammonia increase, ammonia volatilization will similarly increase as Henry's law suggests. This will cause the pH to stabilize and eventually decrease as the rate of ammonia loss becomes greater than that of carbon dioxide (Figure 1.2) [18].

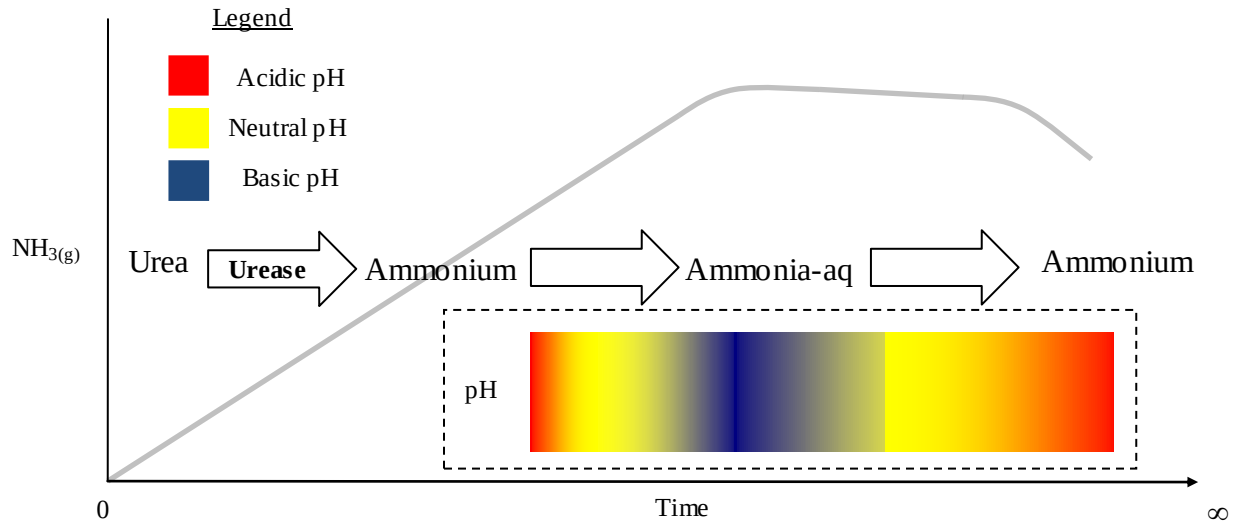

Figure 1.2: The influence of pH on ammonia gas emissions from animal manure (Mechanism 1)

The pH-controlled mechanism is one explanation for the rise in the ammonia gas concentration above manure over time. Another mechanism mentioned in the literature [19] is one controlled solely by the rate of volatilization. Essentially, the rate of ammonia volatilization is exceeded by the formation of aqueous ammonia, resulting in an immediate buildup of aqueous ammonia. As time progresses, the rate of volatilization increases while the rate of aqueous ammonia formation decreases. A peak in the ammonia gas concentration represents the point in

time where ammonia volatilization and aqueous ammonia formation have reached an equilibrium [19]. This mechanism assumes no change in pH.

For the purposes of this thesis, the pH-controlled mechanism will be referred to as Mechanism 1 and volatilization-controlled as Mechanism 2. Knowing which mechanism controls ammonia emissions from a certain manure sample involves a simple observation of ammonia gas concentrations versus time. Mechanism 1 will correspond to a delayed peak, as opposed to Mechanism 2, which will correspond to a peak that occurs relatively quickly.

Mechanisms of Ammonia Flux

Ni et al. [17] describe the pH-controlled mechanism as carbon dioxide accelerated ammonia release (CAAR). Ni et al. [20] developed an empirical model, including several submodels, to predict ammonia emissions from a pig house based on this mechanism. The submodel predicting the carbon dioxide release rate from a pig house used predictor variables including the total pig weight in the house, manure temperature, and building ventilation rate (Equation 1.10). The submodel predicting the ammonia release rate in the pig house used predictor variables including the house floor surface area, manure temperature, ventilation rate, the aqueous ammonia concentration on the manure surface, and the ammonia gas concentration above the manure (Equation 1.11) [20].

$$Q_{Cr} = \frac{1}{3600}\left[(295.5\times10^{-3})W_{tp} + 4.5T_m + \left(232.4\times10^{-3}\right)V - 462.5)\right]$$

Equation 1.10: Carbon dioxide release rate from a pig house as defined by Ni et al. [20]

Where: W_{tp} = total pig weight in the pig house, kg
T_m = manure temperature, ^oC
V = ventilation rate, $m^3\ hr^{-1}$

$$Q_{Ar} = \left(4.78\times10^{-7}\right)\times T_m^{0.8}\times V^{0.7}\times A(C_{Ag,0} - C_{Ah})$$

Equation 1.11: Ammonia release rate from a pig house as defined by Ni et al. [20]

Where: Q_{Ar} = ammonia release rate, $g\ s^{-1}$
A = manure floor surface area, m^2
$C_{Ag,0}$ = aqueous ammonia concentration at the manure surface, $g\ m^{-3}$

C_{Ah} = ammonia gas concentration above the manure, g m^{-3}

$$\delta r = \left(32.8\times10^{-10}\right)\left(\frac{Q_{Cr}}{Q_{Ar}}\right)^2 - (69.5\times10^{-7})\frac{Q_{Cr}}{Q_{Ar}} + 5\times10^{-4}$$

Equation 1.12: Rate of change in the pH of pig manure on a pig house floor as defined by Ni et al. [20]

Where: δr = rate of change in pH, s^{-1}

If the pH of manure on a pig house floor is acidic, the aqueous ammonia concentration at the manure surface will be extremely low. The same applies to any manure slurry. As carbon dioxide is released from the manure, the pH and the aqueous ammonia concentration in the manure rise, thereby increasing the ammonia release rate [17]. This mechanism is a function of Henry's law and is displayed in the submodels developed by Ni et al. [20] (Equation 1.11). Sommer and Sherlock [18] showed that at 16^{o}C and an initial pH of approximately 7, a cattle slurry will experience a rise in pH for 100 hr to a pH of approximately 9. This suggests that the rate of change in pH may be relatively slow, depending on conditions such as temperature and ventilation rate. A peak in the ammonia gas concentration above the manure occurs when the pH stabilizes, or when the effect of carbon dioxide release on pH is offset by the effect of ammonia release. Mechanism 1 explains the observed phenomenon.

Mechanism 2 assumes no change in pH and that the pH is initially basic. Elzing et al. [19] suggest that the rate of urea hydrolysis in a slurry is initially greater than the ammonia release rate, causing a buildup of aqueous ammonia. Sherlock and Goh [12] discovered that the rate of urea hydrolysis is extremely rapid upon exposure to urease with urea half-lives less than 5 hr when applied to soil. As the rate of hydrolysis decreases with the urea concentration, the ammonia release rate eventually exceeds the rate of hydrolysis, depleting aqueous ammonia faster than it can form [19]. This leads to an overall depletion of aqueous ammonia from the manure. From an observation of ammonia gas versus time, a peak in the ammonia gas concentration above the manure occurs when the rate of hydrolysis equals the ammonia release rate.

In summary, all of the studies suggest that the pH-controlled Mechanism 1 corresponds to a delayed peak in gaseous ammonia concentrations, while the volatilization-controlled Mechanism 2 corresponds to one that occurs rapidly.

1.4 Ammonia Fluxes from Dairy Manure

When grazing cattle excrete urine onto soil, urea hydrolysis is complete within a "few" days [21]. However, *complete* hydrolysis is not necessary for ammonia volatilization to occur. In fact, most observations of ammonia emissions from urine on soil show that more ammonia volatilizes in the first day following excretion than in subsequent days. Thus, significant urea hydrolysis occurs following urine application to soil. Muck [10] states that the rate of hydrolysis is a function of the urea concentration. Essentially, when urine is excreted, the urea concentration is high and therefore, hydrolysis is rapid. This leads to an initial buildup of aqueous ammonia in the urine and a high initial spike in ammonia flux. This spike is followed by lower fluxes and slower rates of hydrolysis due to the constant loss of ammonia and lower urea concentrations, respectively.

Soil pH may be acidic or basic. Cattle urine, in most cases, is basic. When urine is applied to soil, a well-mixed solution between the urine and the soil is not created, allowing the urine to remain basic no matter what the soil pH. Therefore, there is essentially no pH-controlled mechanism for ammonia release from cattle urine excreted onto soil. Mechanism 2 more closely describes ammonia volatilization in this situation.

Previous studies have examined ammonia fluxes over time from manure in pastures and soil patches in the laboratory. In two 12-day and two 15-day ammonia volatilization experiments performed by Lockyer et al. [21], between 25 and 60% of the total urinary nitrogen lost was emitted in the first day. For previously mixed or aged slurries, ammonia fluxes were characteristic of those from urine applied to soil. This is consistent with the theory behind Mechanisms 1 and 2 since the pH in aged slurries was likely at a value that is favorable to ammonia mass transfer. Studies performed by Beauchamp et al. [22] showed 24 to 33% of aged cattle slurry TAN was lost to the atmosphere over six to seven day periods following application to soil. And, immediately following application, ammonia volatilization followed a diurnal pattern, similar to that of the ambient temperature. Sommer et al. [23] performed four experiments, each over the course of six days, resulting in accumulated ammonia losses from aged slurries between 45 and 75% of the TAN. In one of the experiments, as much as 30% of the TAN was lost in the first six hours.

A *gradual* rise in ammonia flux to peak over the course of several hours to days is characteristic of fluxes originating from fresh, well-mixed slurries that are initially acidic. Slurries are typically acidic upon mixing of urine and feces because the more acidic feces are excreted at a greater proportion than urine. Though, it should be noted that Mechanism 2 was developed from experiments with urine/feces mixtures and not urine applied to soil. The degree of mixing between the urine and the feces and the urine-to-feces ratio in these experiments likely played a role in the results.

1.5 Dairy Manure Handling Effects on Ammonia Loss

Studies have shown that scraping manure from a barn floor has a minor effect on ammonia emissions from a CAFO [24]. This may be due to scraping equipment's failure to collect the liquid portion of slurries. However, flushing barn floors with water has shown to decrease ammonia emissions by up to 70% [24]. Flush water not only serves the purpose of totally cleaning the barn floor, but dilutes the aqueous ammonia in the slurry, thereby decreasing the ammonia gas concentration in the air above slurry in accordance with Henry's law. However, while ammonia emissions may decrease from the CAFO itself, they may not do so from the entire dairy operation. Flush water will reduce aqueous ammonia concentrations in slurries retained on the barn floor after a flushing event, but it will also increase the volume and surface area of the slurry in another part of the dairy operation.

Manure acidification is one method that has been proven to decrease ammonia emissions in all stages of handling. To examine the effect of sulfuric acid addition to swine manure on ammonia emissions from a pig farm, Kai et al. [25] designed a flushing system to collect and transport manure from a pig house floor to a holding tank. In the holding tank, a 96% sulfuric acid solution was added to the manure at a rate of 0.5 kg acid to every 100 L slurry. Acidified slurry in the tank served as the flush water. Following a flushing event, a layer of slurry (15 cm thick) remained on the floor. Results using this method of acidification showed a 70% reduction in ammonia emissions from the pig house, a 90% reduction from the holding tank, and a 67% reduction from land-applied manure.

Isolating urine from feces is another method that has been researched in a number of studies. One study examined the efficiency of a manure collection system in a pig house

specifically designed to separate solid manure from liquid manure immediately following excretion [26]. Using this system, ammonia concentrations in the pig house averaged 3.2 ppm over a 15-week period and never exceeded 7.5 ppm. Ammonia concentrations in pig houses typically range between 9 and 16 ppm [27].

Decreasing the dry matter content of a slurry will also lower ammonia emissions [28]. This effect only applies to slurries that are land-applied because decreasing the dry matter allows the slurry to better penetrate the soil surface, thereby decreasing ammonia fluxes.

1.6 Dietary Protein Effects on Ammonia Loss

A cow's dietary protein requirements, as a percentage of their diet, decrease as they develop from birth through calving. However, initiation of lactation and the associated demand for nutrients results in increased protein requirements relative to a similar aged animal that is not lactating. Feeding mature, non-lactating cows the same levels of protein as younger cows will result in excess nitrogen in the environment [29]. A mass balance around a cow shows that feeding mature cows less protein could potentially result in less nitrogen in their manure. Henry's law suggests that a reduction in manure nitrogen will lead to a reduction in ammonia emissions from the manure. The challenge is finding a dietary approach that will allow reduced dietary nitrogen while maintaining animal productivity. Several authors have investigated this phenomenon and found encouraging results with respect to ammonia volatilization (Table 1.2).

Table 1.2: Results from studies testing the effect of dietary protein manipulation on nitrogen excretion from cattle and ammonia emissions from cattle manure

Ref.	Low Protein Diet	High Protein Diet	Conclusion Derived from Liquid/Solid Manure Analyses	*p*-value	Conclusion Derived from Manure Gas Analyses	*p*-value
[30, 31]	11.5 %CP[a]	13.0 %CP	Following a feeding period with the low-CP diet, cattle showed a 26% reduction in the mass of excreted urinary nitrogen per day.	0.05	The lower CP diet provided for a 60 to 200% reduction in ammonia volatilization. A regression equation estimating the mass of ammonia lost with urinary nitrogen as a predictor variable had an R^2 value of 0.69. A regression equation estimating the mass of ammonia lost with nitrogen intake as a predictor variable had a significantly low R^2 value of 0.08.	< 0.05
[32]	12.3 %CP	18.3 %CP	Manure pH and TAN were positively correlated to dietary protein levels.	N/A	Ammonia emissions from urine and feces on soil were 0.33 mg N kg^{-1} and 4.99 mg N kg^{-1}, respectively. The proportion of nitrogen lost by ammonia volatilization was lower in the low protein diet. Two different trials were performed in this study. In the first trial, the proportion of TAN lost to the atmosphere as ammonia was not affected by the dietary protein levels, but in the second trial it was.	N/A

Ref.	Low Protein Diet	High Protein Diet	Conclusion Derived from Liquid/Solid Manure Analyses	*p*-value	Conclusion Derived from Manure Gas Analyses	*p*-value
[33]	9.60 %CP	11.0 %CP	Eight heifers were fed two diets varying in their CP levels. There were no apparent differences between the masses of urine and feces excreted following a 12-day feeding period with each diet. Urinary nitrogen, in terms of mass, decreased following a feeding period with the low CP diet (*p*-value < 0.001). The percentage of urinary nitrogen as urea decreased with the low CP diet (*p*-value < 0.01).	< 0.001 and < 0.01	Ammonia fluxes peak 10 to 15 hours following mixing of urine and feces. 42% of nitrogen from slurries was lost through ammonia volatilization. Per head ammonia emissions decreased by 28% following a 14% reduction in nitrogen intake. Ammonia emissions correlated with nitrogen intake with an R^2 value of 0.9101.	< 0.05
[34]	11.5 %CP	13.0 %CP	The low protein diet provided for less nitrogen in excreted urine, on average, and more nitrogen in excreted feces. In observing the total nitrogen excreted in the urine and feces, the low protein diet corresponded to a lower fraction (0.13 lower) of nitrogen in the urine.	N/A	Reducing CP levels in beef cattle diets decreased ammonia fluxes from artificial feedyard surfaces containing manure slurries by 36% in the summer (*p*-value = 0.09), 44% in autumn (*p*-value = 0.04), and 26% in the spring (*p*-value < 0.01). Ammonia fluxes were not affected by dietary CP in the winter. Dietary CP had the greatest effect in the first day following manure application to the feedyard surface.	0.09 and 0.04 and < 0.01

Ref.	Low Protein Diet	High Protein Diet	Conclusion Derived from Liquid/Solid Manure Analyses	*p*-value	Conclusion Derived from Manure Gas Analyses	*p*-value
[35]	13.1 %CP	17.0 %CP	Average TAN concentration of the manure excreted from 20 dairy cows decreased by 62% when the cows were fed a low protein diet. Average mass of TAN excreted in the cattle manure decreased by 33%.	<0.0001	Average ammonia concentration emitted from manure excreted by 20 dairy cows decreased by 58% when cows were fed a low protein diet.	<0.0001
[36]	14.0 %CP	19.0 %CP	N/A	N/A	Manure samples excreted from individual cows over a 24-hour period showed that decreasing CP levels in a cow's diet can decrease ammonia emissions by a factor of ⅔.	0.001

Ref.	Low Protein Diet	High Protein Diet	Conclusion Derived from Liquid/Solid Manure Analyses	*p*-value	Conclusion Derived from Manure Gas Analyses	*p*-value
[37]	12.0 %CP	18.0 %CP	The low protein diet provided for 49% lower urinary total Kjeldahl nitrogen values. There was no apparent correlation between dietary protein and mass of manure excreted. An equation was developed to predict urinary nitrogen excretion using nitrogen intake, dry matter intake, and body weight as predictor variables. The R^2 value for this equation was 0.80.	< 0.05	N/A	N/A
[38]	OEB = 0[b]	OEB = 1000 g cow^{-1} [c]	Cows were fed diets varying in rumen-degradable protein. Total nitrogen in excreted slurries was 11% lower following a feeding period with low protein diet (*p*-value < 0.05). Urea content of the urine decreased 42% following a feeding period with the low protein diet (*p*-value < 0.001).	< 0.05 and < 0.001	Ammonia emissions from manure slurries on the barn floors were 39% lower following a feeding period with the low protein diet.	< 0.001

Ref.	Low Protein Diet	High Protein Diet	Conclusion Derived from Liquid/Solid Manure Analyses	*p*-value	Conclusion Derived from Manure Gas Analyses	*p*-value
[39]	139 g N cow^{-1} d^{-1}	304 g N cow^{-1} d^{-1}	Urea hydrolysis from urine applied to soil was complete within 24 hours. The fraction of urea nitrogen increased with the total nitrogen in the urine.	< 0.001	As a percentage of the total nitrogen, a lower percentage of ammonia was lost to the atmosphere from urine excreted onto soil following a feeding period with the low protein diet. Ammonia released from excreted feces was insignificant.	0.07

[a]CP – Crude Protein
[b](OEB = 0) – the rumen-degradable protein is in balance with the available energy from fermentable organic matter
[c](OEB = 1000 g) – there is a 1000-g surplus of rumen-degradable protein relative to the available energy from fermentable organic matter

2 Design and Validation of a Flux Chamber

For dairy manure analyses, we used a dynamic flux chamber to measure ammonia emitted from the manure. Based on an EPA-approved design, this style of flux chamber is frequently used to establish emission factors, and it is the recommended method for estimating air emissions at Superfund sites [40]. As shown in Figure 2.1, the main structure of the chamber consists of two pieces, one cylinder and one dome, of clear ¼-inch (0.64 cm) thick acrylic (Global Plastics Services International, St. Stephen, New Brunswick, Canada). The design and dimensions used were similar to those recommended in the USEPA User's Guide. The base, or skirt of the chamber, is an acrylic cylinder with a diameter of 18 inches (46 cm), a height of 8.25 inches (21 cm), and a 1.5-inch (3.8 cm) flange around the top. The hemisphere, or dome, is also 18 inches in diameter, with a height of 6 inches (15 cm) and a flange at the base of 1.5 inches. The two pieces connect at the flange using silicone rubber, and the resulting chamber has a volume of approximately 49 L and a sampling area of 254 in^2 (1639 cm^2).

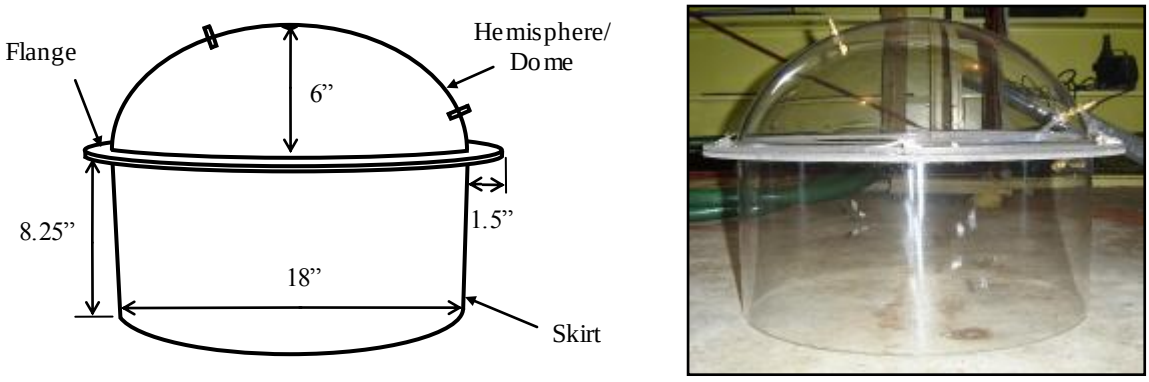

Figure 2.1: Dynamic flux chamber dimensions

The chamber has two ports, one near the apex of the dome for ammonia gas sampling and another near the flange to provide "sweep" air (Figure 2.2). The purpose of the sweep-air is to promote a completely-mixed condition in the headspace of the chamber, above the sample. We chose a sweep-air flow rate of 7 L min^{-1}, the same as used in previous studies with a chamber of similar size and structure [41, 42]. The excess flow was vented through a hole at the apex of the

dome, as the gas sampler did not continuously pull air from the chamber (Figure 2.3). This prevented over-pressurization of the chamber.

Sweep-air must be strictly regulated to measure accurately gaseous emissions with a dynamic flux chamber [40]. Therefore, it was strictly controlled at 7 L min^{-1} using a mass flow controller (Aalborg GFC37). Upstream of the mass flow controller, air passed through tubing whose inlet was placed at least 5 m from the chamber. Isolating the sweep-air inlet from the chamber prevented the sweep-air from being contaminated by ammonia gas vented from the chamber. A diaphragm vacuum pump (Rietschle Thomas 927CA18) pulled ambient air through the tubing and mass flow controller and discharged it to perforated Teflon tubing that wrapped around the chamber at the seam between the dome and the skirt (Figure 2.3). The perforated tubing was held into place with steel wire loops glued into the seam. The perforation in the tubing consisted of four evenly spaced holes with a diameter of 3/32 inches (0.24 cm), with the exception of the first hole which had a diameter of 5/64 inches (0.20 cm) as specified by the USEPA User's Guide. Each of these holes was positioned so the air would flow parallel to the emitting surface and toward the center of the chamber to promote mixing. After wrapping once around the seam of the chamber, the end of the tubing was sealed with a brass cap. An impeller to promote mixing in the chamber has been shown to be unnecessary because it could suppress emissions from the manure and provide another surface on which the ammonia could adsorb [43].

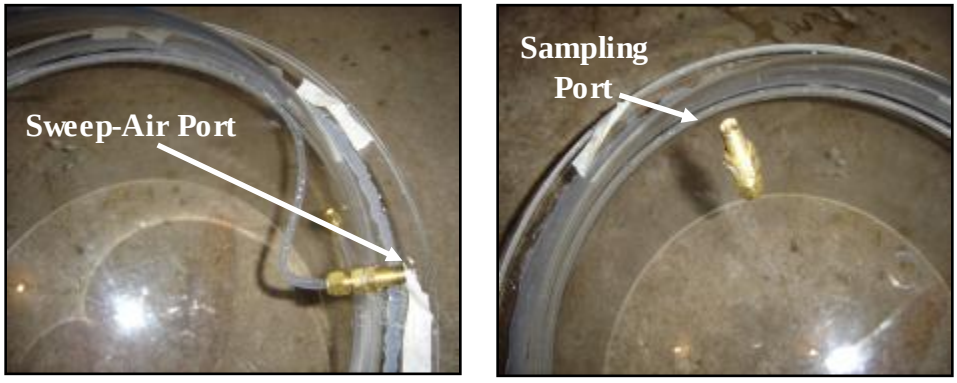

Figure 2.2: Sweep-air and sampling ports on the dynamic flux chamber

All connections were made with ¼-inch OD Teflon tubing and brass Swagelok fittings, except where noted. The use of Teflon versus other materials such as low-density polyethylene (LDPE) minimizes ammonia losses in the system [44].

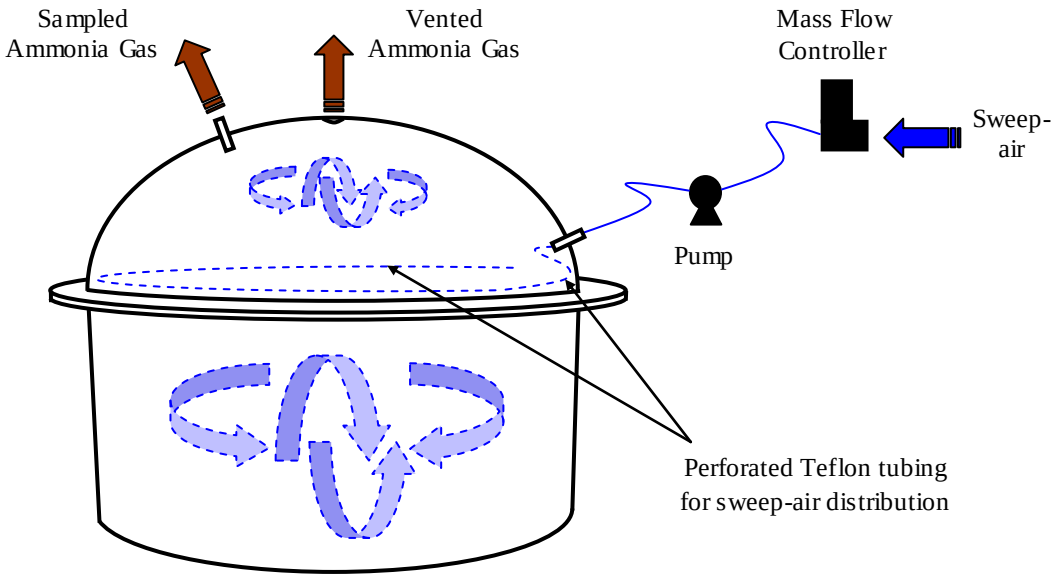

Figure 2.3: Dynamic flux chamber operation

At a sweep-air flow rate of 7 L min^{-1} and a volume of 49 L, the sweep-air had a residence time of 7 min in the chamber. Given that 3.5 residence times signifies a completely-mixed condition, sweep-air was pumped through the chamber for approximately 30 minutes before each experiment to achieve a well-mixed condition [45].

2.1 Photoacoustic Infrared (IR) Analyzer for Ammonia Analyses

The bulk of our ammonia gas measurements were performed with a photoacoustic infrared (IR) analyzer (INNOVA Air Tech Instruments model 1312). The analyzer was calibrated for ammonia gas and water vapor by California Analytical (Orange, CA) before use in our studies and again after 1 yr.

The photoacoustic analyzer measures ammonia gas by first drawing a sample of air through tubing at the rear of the instrument. Upon entering the analyzer, the air sample passes through two filters, which remove any dust and particulates that may otherwise cause error or damage. Once filtered, the air sample is contained within an analysis cell inside the instrument. A beam of infrared light passes through a mechanical chopper and then through an optical filter

that is specific for the wavelength at which ammonia absorbs. The mechanical chopper serves the purpose of pulsating the infrared light, so that the temperature of the ammonia gas is constantly increasing and decreasing. The resulting change in pressure produces an acoustic signal, which is measured by two ultra-sensitive microphones in the walls of the analysis cell. The signal is directly proportional to the concentration of ammonia gas in the sample. The intensity of the signal is relayed from the microphones to the instrument display, which reports the concentration of ammonia gas in units of mass per volume [46].

The analyzer samples at intervals chosen by the user. For the majority of this study, the analyzer was programmed to sample once every three minutes. During each sampling event, the sampling pump draws enough volume to flush the sample tubing and collect a sufficient volume of sample for analysis. The sampling pump pulls air at a flow rate of 2 L min^{-1}.

Water vapor may cause interference in measurements with photoacoustic analyzers. Therefore, we chose the option of compensating for water vapor in our ammonia gas measurements. The instrument has a detection limit of 1.4 x 10^{-7} mg m^{-3}.

2.2 Dynamic Flux Chamber Validations

Due to ammonia's ability to readily adsorb to surfaces, our dynamic flux chamber had to be validated to determine what percentage of the ammonia emitted from the manure sample actually exited the chamber, and what percentage was retained on the interior surfaces of the chamber. We tested three different analytical methods for determining gaseous ammonia concentrations: (1) a photoacoustic ammonia analyzer, (2) collection of ammonia on diffusion denuders followed by extraction, distillation, and titration, and (3) trapping in a boric acid indicator solution. For each method, we conducted a blank measurement to determine ammonia concentrations in the background air and then a second set of measurements involving the volatilization of a known amount of ammonia from an aqueous solution into the chamber. Through a mass balance between the amount volatilized and the amount measured in the gaseous phase, we could then calculate the percent recovery of ammonia.

Photoacoustic Analyzer Validations

The first method we used to validate the dynamic flux chamber employed the photoacoustic analyzer. We performed the photoacoustic analyzer validations in a laboratory located at the Virginia Tech Dairy. Before validating the chamber, we performed a blank measurement to determine background ammonia concentrations in the laboratory. In every test, the mass flow controller for the sweep-air was "zeroed" before each validation by allowing it to equilibrate for approximately 30 minutes. If the controller did not read zero after equilibration, it was adjusted to read zero.

After starting the pump and ammonia analyzer and allowing the chamber to reach a well-mixed state, we began measuring ammonia gas concentrations every two minutes for 60 min with the photoacoustic analyzer. Figure 2.4 shows NH_3 concentration time series for the blank experiment.

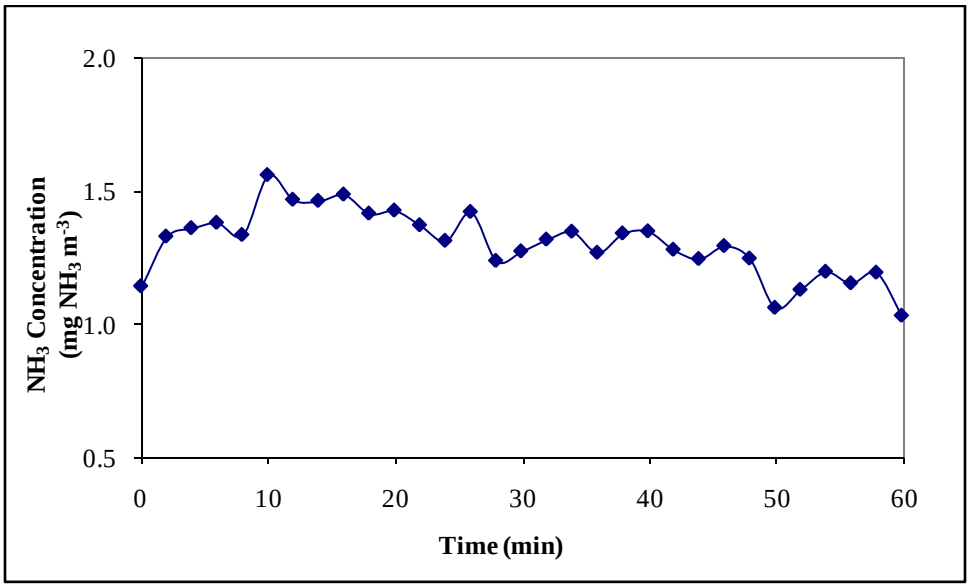

Figure 2.4: Background ammonia concentrations at the Virginia Tech Dairy laboratory

The blank analysis showed an average background ammonia concentration of 1.30 mg m^{-3}. In the analysis, we also determined the total mass of ammonia pumped into the chamber from the ambient air over a 60-min period (Equation 2.1). Using air from the Virginia Tech Dairy laboratory as influent sweep-air to the chamber, 0.550 mg of ammonia was pumped into the chamber over a 60-min period.

$$\{\sum_{1}^{i_f-1}[(\frac{C_i+C_{i+1}}{2} \times (t_{i+1} - t_i)) \times Q_{Sweep}]\} \times \frac{14}{17{,}000} = M_{NH_3\text{-Blank}}$$

Equation 2.1: Mass of ammonia pumped in the dynamic flux chamber during a blank measurement with the photoacoustic analyzer

Where: C_i = number i ammonia concentration in a sequence of concentrations logged in the memory of the photoacoustic analyzer from a blank measurement, mg NH_3 m^{-3}
C_{i+1} = final ammonia concentration in a sequence of concentrations logged in the memory of the photoacoustic analyzer from a blank measurement, mg NH_3 m^{-3}
t_i = time when C_i was recorded in the memory of the photoacoustic analyzer, hr:min:sec
Q_{Sweep} = sweep-air flow rate, 7 L min^{-1}
$M_{NH_3\text{-Blank}}$ = mass of ammonia-nitrogen lost during a blank measurement performed with the photoacoustic analyzer, mg N

In performing the validations, the photoacoustic analyzer and the dynamic flux chamber were set up in the same manner as they were for the blank measurement. However, we performed a few additional steps to validate the chamber. First, we allowed the conditions inside the chamber to approach a completely-mixed condition by pumping in sweep-air for approximately 30 min. Second, we prepared a buffered ammonium (NH_4^+) solution (428 mg NH_4^+ L^{-1}) in a 1-L volumetric flask. The solution contained 0.087 mol L^{-1} tripotassium phosphate (K_3PO_4), 0.013 mol L^{-1} of monopotassium phosphate (KH_2PO_4), and 0.01 mol L^{-1} of a 50% sodium hydroxide (NaOH) solution in water. Then, we poured 400-500 g of the NH_4^+ solution from the flask into a 21.6 cm × 16.5 cm plastic tray. We measured and recorded the mass of the contents in the tray. Then, we placed the tray and an underlying Teflon sheet underneath the chamber. The purpose of the Teflon sheet was to minimize ammonia adsorption to the exposed surface around the tray (Figure 2.5).

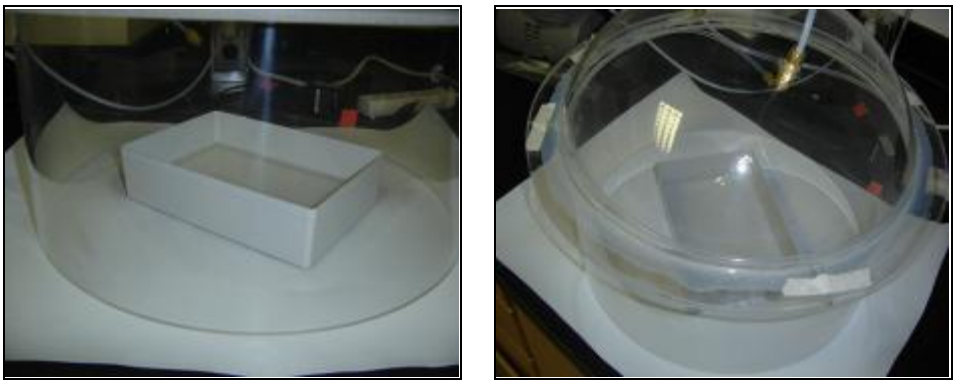

Figure 2.5: Placement of tray and Teflon sheet for validations

Once the tray was placed underneath the chamber, we began measuring ammonia gas concentrations inside the chamber every two minutes for 60-74 min with the photoacoustic analyzer. Immediately after we began measurements, we sub-sampled 10 mL of the remaining ammonium solution in the 1-L volumetric flask into a glass 20-mL vial. We acidified the sub-sample with a small, arbitrary amount of concentrated sulfuric acid (H_2SO_4) (< 5 drops with a 1-mL pipettor). Following acidification, we capped the vial, sealed it with Parafilm, and stored it at 4^{o}C. Within one week of sampling, we tested the contents of the vial for ammonia by distillation and titration per Standard Methods for the Examination of Water and Wastewater, Methods 4500-NH_3 B and C [47].

Just after the last measurement with the photoacoustic analyzer, we removed the tray from underneath the chamber and then measured and recorded the mass of its contents. We used a 10-mL pipette to sub-sample 10 mL of the buffered ammonium solution from the tray. We used the same procedure to acidify, store, and analyze the sample from before the validation for the sample after the validation.

The distillation and titration procedure provided us with the mass of TAN in the tray, before and after the validation, thereby providing us with mass of TAN lost from the tray during the validation (Equation 2.2). The sweep-air flow rate and the data provided by the photoacoustic analyzer provided us with the mass of TAN emitted from the chamber during the validation (Equation 2.3).

$$C_0 \times \frac{M_0}{\rho_{Water}} - C_f \times \frac{M_f}{\rho_{Water}} = M_{NH_3\text{-}Tray}$$

Equation 2.2: Mass of ammonia-nitrogen lost from the tray underneath the chamber during a validation (solution analysis)

Where: C_0 = TAN concentration in the tray before the validation, mg N L^{-1}
C_f = TAN concentration in the tray after the validation, mg N L^{-1}
M_0 = mass of solution in the tray before the validation, mg
M_f = mass of solution in the tray after the validation, mg
ρ_{Water} = density of water, 10^6 mg L^{-1}
$M_{NH_3\text{-}Tray}$ = mass of ammonia-nitrogen lost determined by solution analysis, mg N

$$\{[\sum_{1}^{i_f-1}((\frac{C_i+C_{i+1}}{2} \times (t_{i+1} - t_i)) \times Q_{Sweep}] \times \frac{14}{17{,}000}\} - M_{NH_3\text{-}Blank} = M_{NH_3\text{-}Photoacoustic}$$

Equation 2.3: Mass of ammonia-nitrogen lost from the tray underneath the chamber during a validation (photoacoustic analysis)

Where: C_i = number i ammonia concentration in a sequence of concentrations logged in the memory of the photoacoustic analyzer from a validation, mg NH_3 m^{-3}
C_{i_f} = final ammonia concentration in a sequence of concentrations logged in the memory of the photoacoustic analyzer from a validation, mg NH_3 m^{-3}
$M_{NH_3\text{-}Photoacoustic}$ = mass of ammonia-nitrogen lost during a validation performed with the photoacoustic analyzer, mg N

Figure 2.6, Figure 2.7, and Figure 2.8 show NH_3 concentration vs. time for three validation experiments. All three of the validations performed with the photoacoustic analyzer showed concentrations in the chamber headspace near 100 mg m^{-3}. This concentration is of the same order of magnitude as the concentrations we measured from the manure.

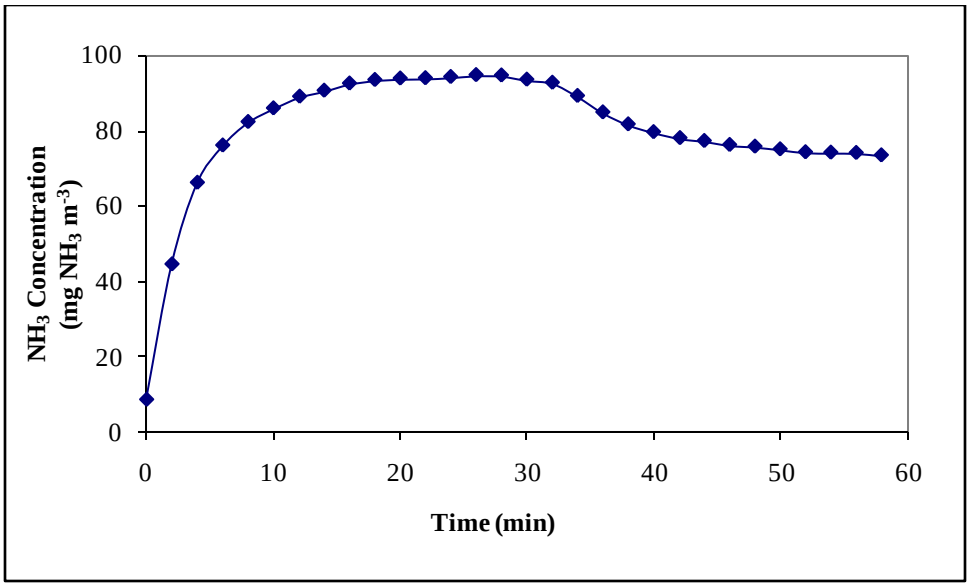

Figure 2.6: Ammonia concentrations in the chamber headspace during a validation performed with the photoacoustic analyzer, 2/26/2007

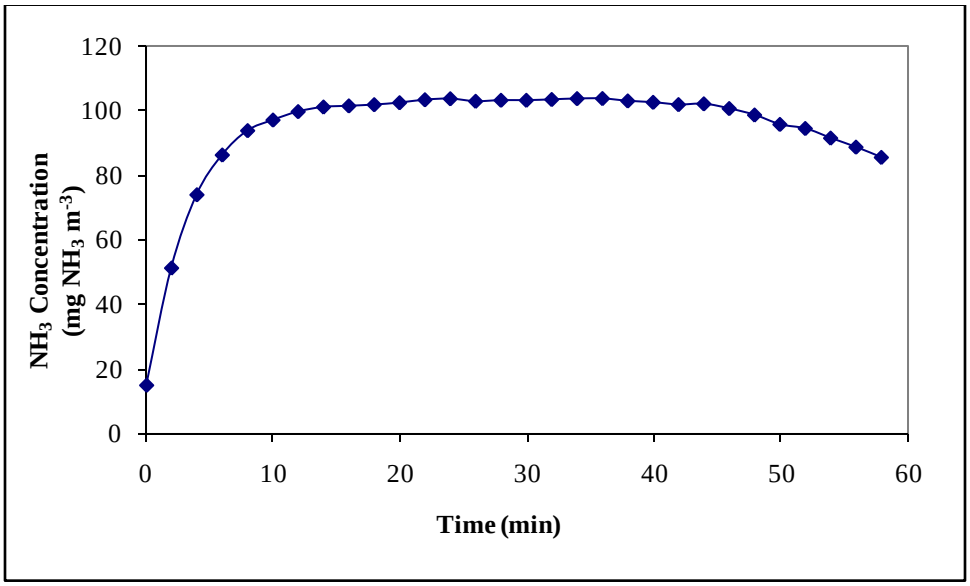

Figure 2.7: Ammonia concentrations in the chamber headspace during a validation performed with the photoacoustic analyzer, 2/26/2007-2

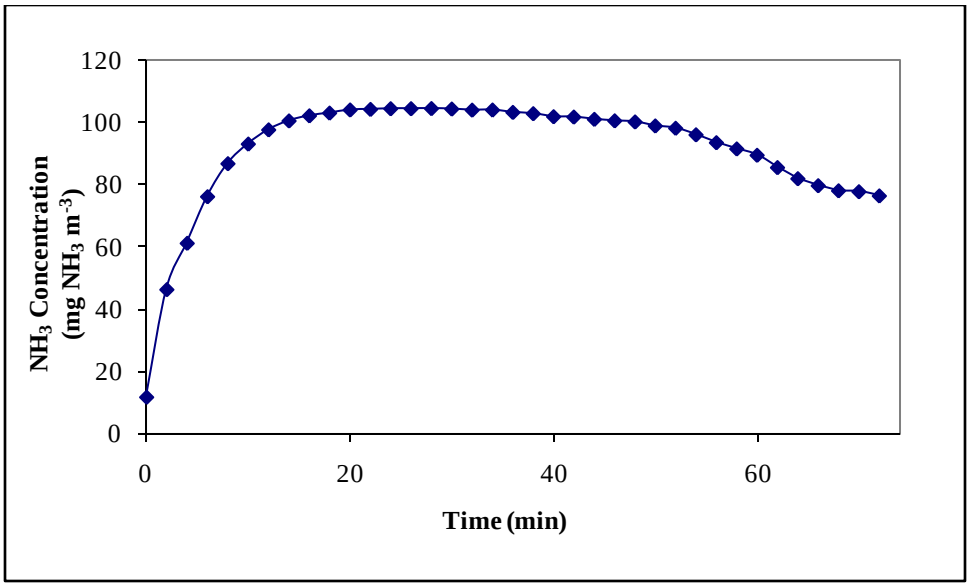

Figure 2.8: Ammonia concentrations in the chamber headspace during a validation performed with the photoacoustic analyzer, 2/27/2007

After performing the validations and analyzing all of the data using Equation 2.2 and Equation 2.3, we calculated a "percent recovery" (Equation 2.4).

$$\frac{M_{NH_3\text{-Photoacoustic}}}{M_{NH_3\text{-Tray}}} \times 100\% = \%\ \text{rec.}$$

Equation 2.4: Percent recovery from the dynamic flux chamber by photoacoustic analysis

Where: % rec. = percent recovery, %

The % rec. results are shown in Table 2.1. The average % rec. was 112±8% (mean±standard deviation). The difference from 100% is within the expected uncertainty of the analytical procedures and methods. We expected that the percent recoveries would be below 100% due to ammonia's ability to readily adsorb to surfaces. Real recoveries of greater than 100% are possible if conditions in the chamber were not completely mixed and some short-circuiting occurred. The encouraging conclusion that may be drawn from these results is that ammonia adsorption on the interior surfaces of the chamber appears to be negligible, and if any short-circuiting did occur, it did not affect the results by more than ~10%.

Table 2.1: Percent recoveries for validations performed with the photoacoustic analyzer

Date	% rec.
2/26/2007	114%
2/26/2007-2	103%
2/27/2007	118%

Denuder Validations

The second method we used to validate the chambers used diffusion denuders (URG, Chapel Hill, NC) (Figure 2.9). The denuders contain either two or three concentric etched glass cylinders, providing for either three or four interior flow channels, respectively. The interior surfaces of the denuder are usually coated with an adsorbent for the compound of interest.

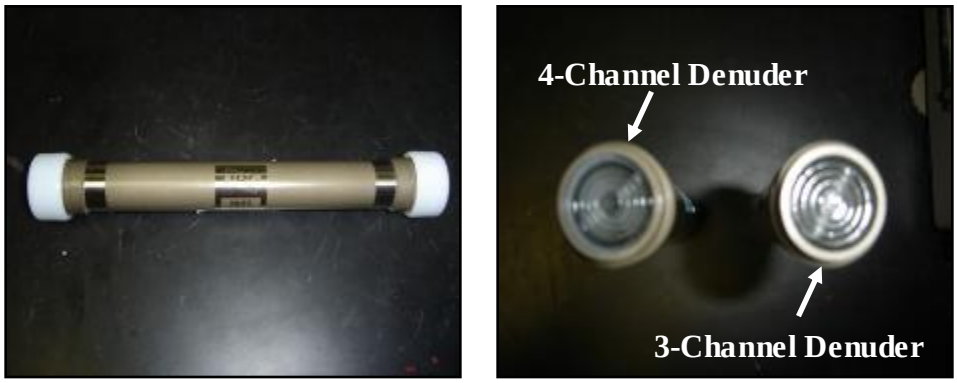

Figure 2.9: Denuders for ammonia gas analysis

We performed denuder validations in a laboratory located in an academic building isolated from the dairy. We did not perform a blank measurement for the denuder validations because we found background ammonia concentrations to be insignificant, even at the Virginia Tech Dairy where concentrations are expected to be high. Aside from changing the location of the validations, we also adjusted the validation procedure used with the photoacoustic analyzer to facilitate the procedure.

To clean the denuders, we rinsed them five times with deionized water and then once with methanol. We dried them by running compressed breathing air through them for approximately 60 s. We then coated the denuders with a 1% citric acid, 50/50 methanol/deionized water solution, dried them again, capped, and sealed them with Parafilm until testing.

For analysis with the flux chamber, we connected three denuders of equal interior surface area in series to the flux chamber on one end and a vacuum pump on the other end (Figure 2.10). We connected the discharge end of the pump to a mass flow controller set at a flow rate of 0.5 L min^{-1}. We used a second vacuum pump and mass flow controller to deliver sweep-air to the chamber at a flow rate of 7 L min^{-1} (Figure 2.10).

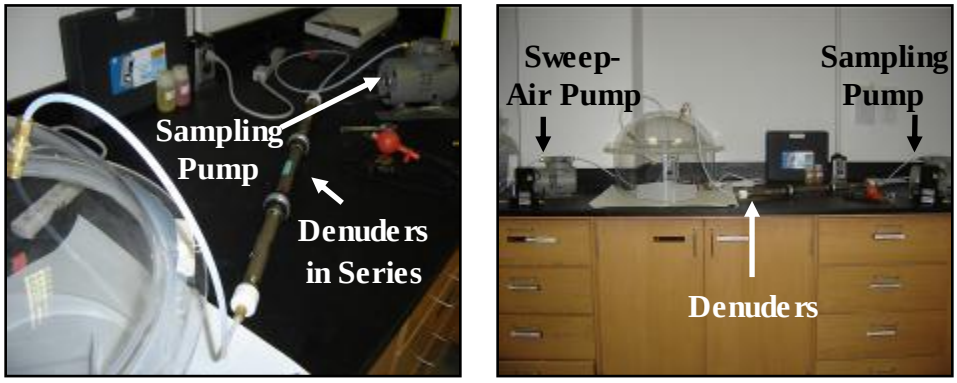

Figure 2.10: Placement of denuders for ammonia gas sampling

Once the conditions inside the chamber were fully mixed, we poured 400-500 g of a 500 mg L^{-1} stock solution of NH_4^+, with no buffer components, into a plastic tray. Following the same procedure described above, we sub-sampled the solution, acidified, stored, and analyzed it.

To begin the validation, we added 1 mL of 45% potassium hydroxide (KOH) solution to the tray. We measured and recorded the mass of the contents in the tray. Then, we placed the tray and an underlying Teflon sheet underneath the chamber. After adding the KOH to the ammonium solution, we very quickly placed the tray underneath the chamber. We then turned on the pump connected to the denuders and ran it for 30 min. At the end of the sampling period, we removed the tray, recorded its mass, and added 0.5 mL of concentrated H_2SO_4. We sub-sampled 10 mL of the NH_4^+ solution from the tray and used the same procedure described above to store and analyze the sample.

Upon removing the denuders from the sampling train, we capped and sealed them with Parafilm until extraction. To extract them, we added 10 mL of deionized water to the denuders through the flow-straightening (recessed) end, with the other end still capped. Then, we resealed the flow-straightening end and manually inverted the denuder multiple times. We then poured the extract into a 20-mL vial, acidified, stored, and analyzed the sample for ammonia.

The distillation and titration provided us with the mass of TAN in the tray, before and after the validation, thereby providing us with mass of TAN lost from the tray during the validation (Equation 2.2). By knowing $M_{NH3\text{-}Tray}$ and the total volume of air exhausted from the chamber during the validation, we were able to calculate the average ammonia concentration in the chamber during the validation. We used this value to calculate an expected TAN mass in the denuders (Equation 2.5). We compared the expected TAN mass in the denuders to what we determined from the denuder extract in the laboratory by distillation and titration (Equation 2.6).

$$\frac{M_{NH_3\text{-}Tray}}{Q_{Sweep} \times t} \times Q_{Denuders} \times t = \text{Expected } M_{NH_3\text{-}Denuders}$$

Equation 2.5: Mass of ammonia-nitrogen in the denuders by solution analysis

Where: $Q_{Denuders}$ = denuder flow rate, 0.5 L min^{-1}
t = duration of validation, 30 min
Expected $M_{NH_3\text{-}Denuders}$ = expected mass of ammonia-nitrogen in all three denuders determined by solution analysis, mg N

$$\frac{\text{Actual } M_{NH_3\text{-}Denuders} \times {}^{10}/_{8}}{\text{Expected } M_{NH_3\text{-}Denuders}} \times 100\% = \%\text{ rec.}$$

Equation 2.6: Percent recovery from the dynamic flux chamber by denuder analysis

Where: Actual $M_{NH_3\text{-}Denuders}$ = actual mass of ammonia-nitrogen in all three denuders determined by denuder extract analysis, mg N
${}^{10}/_{8}$ = factor to account for the 2 mL of extract that was retained in the denuders during the extraction process. It should be noted that acquiring the full 10 mL of extract was not possible.

The results from using Equation 2.6 are shown in Table 2.2. The average % rec. was 106±24%. The results from the denuder validations are not significantly different from the results using the photoacoustic analyzer and further suggest that correction for deposition losses in the chamber is not needed.

Table 2.2: Percent recoveries for validations performed with the denuders

Date	% rec.
5/16/2007	111%
5/16/2007	103%
5/16/2007	75.5%
5/16/2007	134%

We observed ammonia only in the first and second denuders in series, never in the third denuder, and we always observed the highest concentration of ammonia in the first denuder in series.

Acid Trap Validations

For the acid trap validations, we placed two 500-mL Pyrex flasks in series at the sampling port of the chamber. For each acid trap validation, we placed 300 mL of indicating boric acid in each flask. We prepared the indicating boric acid per Standard Methods for the Examination of Water and Wastewater, Methods 4500-NH_3 B and C [47]. Glass tubing penetrated the stopper at the top of each flask and extended into the boric acid with one end connected to a diffusion stone and the other end connected to ¼-inch OD Teflon tubing. We placed a Teflon disc above the diffusion stone, perpendicular to the flow of air in the boric acid, to create an obstacle for air bubbles as they traveled to the surface of the boric acid and maximize their residence time (Figure 2.11).

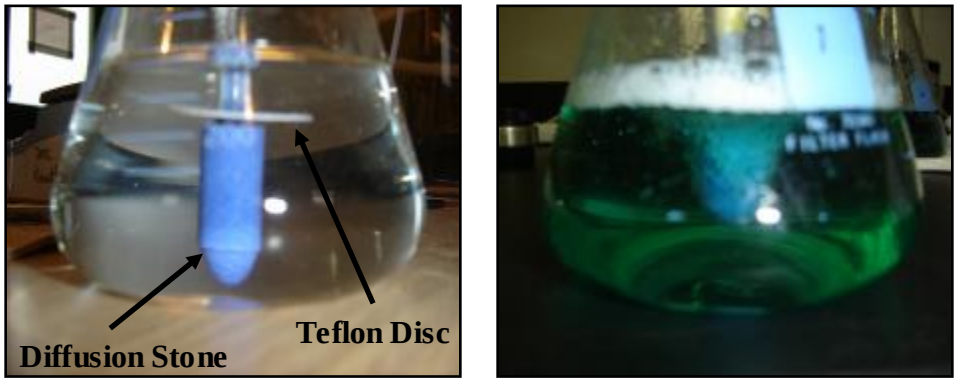

Figure 2.11: Indicating boric acid traps: placement of diffusion stone and Teflon disc

We encountered significant noise with this validation method, and multiple blank measurements, diffusing laboratory air in the boric acid, were required to determine the signal

from the validations with ammonia-laden air. We hypothesized that the noise was due to changes in the carbonate system and not from high background ammonia concentrations.

We performed all blank measurements and validations with the acid traps in a laboratory located in an academic building isolated from the dairy. The sampling train consisted of the chamber, two acid traps in series, a vacuum pump, and then a mass flow controller set at 0.5 L min^{-1} (Figure 2.12). We used a second pump to deliver sweep-air to the chamber at a flow rate of 7 L min^{-1}.

Figure 2.12: Placement of acid traps for ammonia gas sampling

To begin the blank measurement, we turned on the pump connected to the flasks, allowing laboratory air to diffuse into the boric acid for 30 min. As the test progressed, the color of the boric acid transitioned from pale lavender to dark green. After 30 min, we turned off the pump. Then, we sub-sampled 100 mL of boric acid from each flask and titrated the sub-sample back to the original pale lavender color with 0.1 N H_2SO_4. The acid was standardized and the titration was performed per Standard Methods for the Examination of Water and Wastewater, Method 2320B.3b and Methods 4500-NH_3 C [47], respectively. We multiplied the volume used for the titration of the 100 mL sub-sample by three to extrapolate back to the original 300 mL volume in the flask.

To determine the standard amount of noise that we would encounter in the acid trap validations, we converted the total volume of sulfuric acid used in the titration of both flasks to a mass of ammonia, as if the color change was due solely to background ammonia gas in the laboratory. We performed this conversion so that we could simply subtract the mass determined from the blank measurement from the mass of ammonia-nitrogen determined in the validations.

We performed the acid trap validations in the same manner as the denuder validations. At the end of the validation, we sub-sampled 100 mL from each flask and performed titrations in the exact same manner as the blank measurement.

We compared the expected TAN mass in the acid traps to what we determined from the titrations (Equation 2.8).

$$\frac{M_{NH_3\text{-Tray}}}{Q_{Sweep} \times t} \times Q_{Acid\ Traps} \times t = \text{Expected } M_{NH_3\text{-Acid Traps}}$$

Equation 2.7: Mass of ammonia-nitrogen in the acid traps by solution analysis

Where: $Q_{Acid\ Traps}$ = acid trap flow rate, 0.5 L min^{-1}
Expected $M_{NH_3\text{-Acid Traps}}$ = expected mass of ammonia-nitrogen in both acid traps determined by solution analysis, mg N

$$\frac{\text{Actual } M_{NH_3\text{-Acid Traps}} - M_{NH_3\text{-Blank}}}{\text{Expected } M_{NH_3\text{-Acid Traps}}} \times 100\% = \%\ \text{rec.}$$

Equation 2.8: Percent recovery from the dynamic flux chamber by acid trap analysis

Where: Actual $M_{NH_3\text{-Acid Traps}}$ = actual mass of ammonia-nitrogen in both acid traps determined by titration, mg N

The % rec. results are shown in Table 2.3. The average % rec. was 47.0±37.1%. The acid trap validations showed considerable variation between the two tests, probably due to the noise experienced with this method. The results also do not agree with the results from either of the previous methods.

Table 2.3: Percent recoveries for validations performed with the acid traps

Date Validation Performed	% rec.
5/16/2007	20.7%
5/16/2007	73.2%

Validation Summary

Both the photoacoustic analyzer and the denuders could be used to sample ammonia gas accurately, and validation results using these two methods agreed. The percent recoveries were not significantly different from 100%, suggesting that loss of ammonia to the interior surfaces of the chamber is not significant. The method involving the boric acid traps produced an unacceptable amount of uncertainty (47.0±37.1%). Therefore, we excluded this method in determining the overall percent % rec. from the chamber. Indicating boric acid traps have been used successfully in the past in similar analyses [33]. Additionally, we understand there are certain measures that could have been taken to achieve better results such as increasing the strength of the NH_4^+ solution underneath the chamber or lowering the strength of the H_2SO_4 used in the titration. Despite the effects these changes may have had on the results, for future analyses with acid traps, we recommend using a sulfuric acid solution in the flasks, sub-sampling the solution at the end of the validation from each flask, and distilling and titrating the sub-samples to determine the ammonia content [32]. Refer to Standard Methods for the Examination of Water and Wastewater, Methods 4500-NH_3 B and C.

To calculate a single average % rec. from the chamber, we combined the data from the two validation methods and generated a boxplot to determine any outliers (Figure 2.14). We removed the outliers from the data and calculated an average % rec. along with a standard deviation and coefficient of variation. The resulting average % rec. was 114±11%.

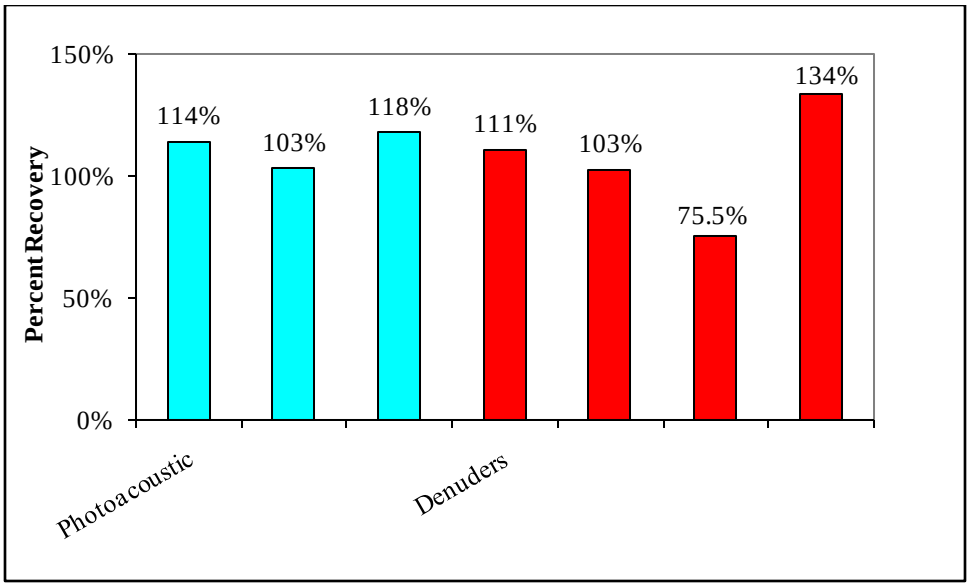

Figure 2.13: Percent recoveries for validations performed with the photoacoustic analyzer and the denuders

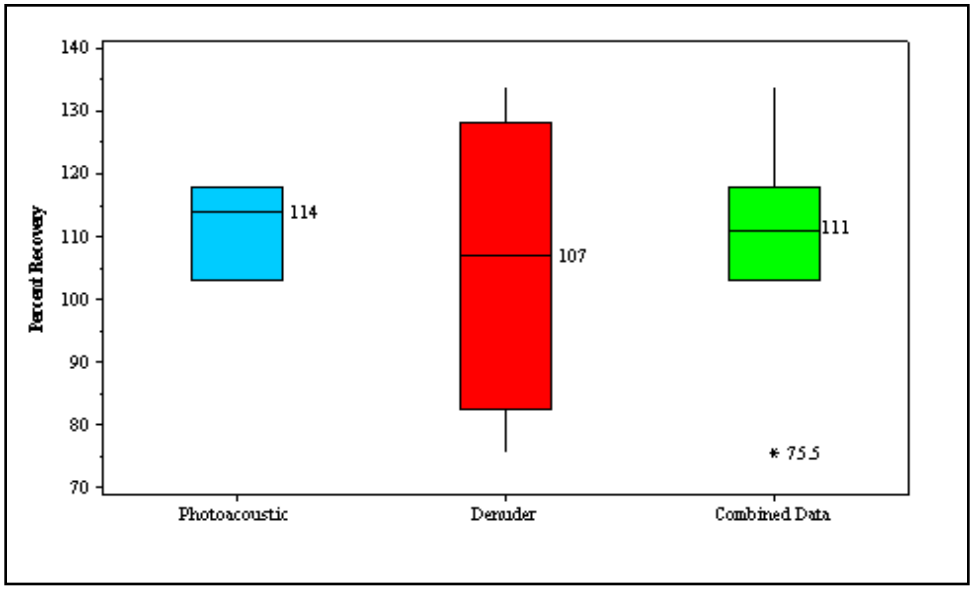

Figure 2.14: Boxplot to determine the outliers from the photoacoustic analyzer/denuders combined data

3 The Effects of Manure Handling and Dietary Protein on Ammonia Emissions from a Flush Dairy

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Abstract

One of the largest sources of atmospheric ammonia, a key ingredient in the formation of some airborne particulate matter, is dairy cattle excreta. Reduction in dietary protein intake by dairy cows has the potential to reduce ammonia emissions from concentrated animal feeding operations (CAFOs). An improved understanding of the relationship between diet and ammonia emissions as a function of manure handling is needed for the development of models that can predict ammonia fluxes from CAFOs and the development of science-based strategies for reducing ammonia emissions associated with dairy cattle. In this study, seven lactating Holstein cows were subjected to four feeding trials with diets containing 14.5, 15.5, 17 and 18% crude protein (CP). The first objective was to determine the effect of protein content/intake on ammonia fluxes from each of four stages of manure handling—scrape, flush, separated solids, and separated liquids—at a dairy. The second objective was to examine the effect of manure handling itself on ammonia fluxes. While ammonia fluxes from the scraped and flushed manure were low initially and rose gradually over the course of a day, fluxes from the separated solids and liquid manure rose immediately and then stayed relatively constant. The contrasting temporal patterns of fluxes may stem from differences in the average pH of the manure, 6.87±0.17 and 7.05±0.13 in the scraped and flushed manure, respectively, versus higher values of 8.70±0.30 and 8.55±0.19 in the separated solids and separated liquids, respectively. Multivariable regressions predicting the mass of ammonia lost to the atmosphere as a function of total ammoniacal nitrogen (TAN) and temperature (T) show that fluxes from the scraped and

flushed manure are very sensitive to temperature compared to the separated solids and liquid manure. The same regressions show that ammonia fluxes from the separated solids and liquid manure are predicted well by TAN and T (R^2 = 0.906 and 0.812, respectively), indicating that dietary protein manipulation, which affects TAN content of the manure, may have a greater effect in this stage of handling. Crude protein intake by itself, however, is a poor predictor of the overall ammonia flux from a flush dairy.

3.1 Introduction

Mainly due to its ability to form fine particulate matter, defined as particles with diameters smaller than 2.5 μm ($PM_{2.5}$), atmospheric ammonia has the potential to be detrimental to human health, the economy, and the environment. In the eastern US, the majority of $PM_{2.5}$ is composed of ammonium nitrate (NH_4NO_3) and ammonium sulfate ($[NH_4]_2SO_4$). Both compounds form via heterogeneous reactions involving precursor gases: sulfur dioxide (SO_2), nitric oxides (NO_x), and ammonia (NH_3). SO_2 and NO_x have been studied extensively and several technologies capable of reducing emissions of these compounds have been developed [1]. However, the more dispersed sources of ammonia make its emissions harder to control. Developing strategies for ammonia control is important because ammonia is the limiting factor in secondary $PM_{2.5}$ formation in some areas [2].

Livestock manure is estimated to contribute 80% of the ammonia emitted to the atmosphere [1], and dairy cattle are a major component of livestock manure emissions. On a per animal basis, they contribute more ammonia to the atmosphere than all other grazing domesticated animals [3]. From a broader perspective, all cattle, including dairy, are responsible for approximately 50% of the agricultural ammonia emitted each year [3, 4].

The majority of atmospheric ammonia emitted from cattle manure is initially present in the urine in the form of urea ($CO(NH_2)_2$) [9]. On average, only 3% of nitrogen in cow urine is present as ammonia-nitrogen following excretion, while approximately 70% exists as urea. The other 27% consists of allantoin, hippuric acid, creatinine, creatine, and uric acid. When urine comes in contact with the urease enzyme, urea is hydrolyzed to form the ammonium ion (NH_4^+) (

Equation 3.1: Urea hydrolysis [4]

) [4].

$$CO(NH_2)_2 + 3H_2O \xrightarrow{\text{Urease}} 2NH_4^+ + HCO_3^- + OH^-$$

Equation 3.1: Urea hydrolysis [4]

The urease enzyme is naturally present in bovine feces. The rate of hydrolysis is a function of several factors including temperature, pH, and substrate (urea) concentration [10]. The rate has been described by first-order [11] as well as Michaelis-Menten kinetics [10].

Following urea hydrolysis, NH_4^+ is converted to aqueous ammonia ($NH_{3(aq)}$) according to general acid/base equilibrium with a pK_a of 9.25 at 25°C. The equilibrium between dilute aqueous (< 1000 mg $NH_{3(aq)}$ L^{-1}) and gaseous phase ammonia can be characterized by Henry's law [13]. Henry's law constant ranges between 5.39×10^{-4} and 9.35×10^{-4} at 25ºC (dimensionless, defined as $C_{NH_{3(g)}} / C_{NH_{3(aq)}}$) [11, 14-16, 23, 48-51].

An improved understanding of the variables affecting ammonia fluxes from dairy cattle manure is required in order to reduce emissions from this source systematically. Fluxes will vary considerably depending on a number of factors including manure temperature, age, pH, concentration, and wind speed at the manure-air interface [23]. Fluxes from cattle urine applied to soil are typically characterized by high initial values immediately following application,

proceeded by lower values as time progresses [21]. This behavior suggests that initial rates of urea hydrolysis are high and initial pH values favorable to ammonia mass transfer to the gaseous phase. Aged cattle manure slurries (urine/feces mixtures) have been shown to exhibit similar patterns of ammonia loss as well [22, 23].

Limited data exists on ammonia fluxes from fresh cattle manure slurries and the effect of manure handling on fluxes from this source. A study performed by Kroodsma et al. [24] suggests that the potential to control emissions is greatest in a concentrated animal feeding operation (CAFO) rather than in the field. The time between excretion of manure and its final stage of handling is especially critical. Typical handling methods of fresh manure in CAFOs include manually scraping it from the barn floor and flushing it from the barn floor with water. Compared to scraping, flushing has been shown to decrease ammonia emissions from a feeding operation due to a more thorough cleaning and dilution of aqueous ammonia in the slurry retained on the barn floor [24]. While ammonia emissions from the barn floor may decrease, the total flux from the manure handling process may not due to an increase in volume and surface area of the slurry in another part of the operation.

Other studies have examined manure acidification as a means for reducing ammonia emissions from agricultural operations. To examine the effect of sulfuric acid addition to swine manure, Kai et al. [25] designed a flushing system to collect and transport manure from a pig house floor to a holding tank. In the holding tank, a 96% sulfuric acid solution was added to the manure at a rate of 0.5 kg acid to every 100 L slurry. Acidified slurry in the tank served as the flush water. Following a flushing event, a layer of slurry (15 cm thick) remained on the floor. This approach resulted in a 70% reduction in ammonia emissions from the pig house, a 90% reduction from the holding tank, and a 67% reduction from land-applied manure.

Isolating urine from feces is another strategy for reducing ammonia emissions. One study examined the efficiency of a manure collection system in a pig house specifically designed to separate urine from feces immediately following excretion [26]. Using this system, ammonia concentrations in the pig house averaged 3.2 ppm over a 15-week period and never exceeded 7.5 ppm. Ammonia concentrations in pig houses typically range between 9 and 16 ppm [27].

McCubbin et al. [2] showed that the optimal method for controlling emissions is to attack the problem before the manure is even excreted by manipulating dietary protein. Reducing dietary protein reduced the urea/nitrogen content in the urine, thereby reducing urease activity, urea availability, and ammonia gas formation [37, 38]. A number of previous studies have shown that a reduction in urinary nitrogen corresponds to a reduction in ammonia emissions. Reducing the percentage of crude protein (% CP) from 13 to 11.5% CP resulted in a 60 to 200% reduction in ammonia emissions from a beef cattle feedyard [31]. Laboratory experiments with dairy cattle manure (5 g feces and 3.9 mL of urine, mixed) have shown that a 14% reduction in nitrogen intake results in a 28% reduction in ammonia loss from manure slurries [33]. Another study, performed on a larger scale, showed that reducing dietary protein from 17.0 to 13.1% CP reduces ammonia emissions from manure channels behind feeding pens by 58% [35]. Together, these studies suggest that a reduction in dietary protein will result in a reduction in ammonia emissions from a CAFO as a whole. Still, an improved understanding of the relationship between diet and ammonia emissions as a function of manure handling is needed for the development of models that can predict ammonia fluxes from CAFOs and the development of science-based strategies for reducing ammonia emissions associated with dairy cattle.

3.2 Objectives

The first objective of this study is to examine ammonia fluxes from fresh cattle manure slurries as a function of different manure handling methods typically employed at dairy farms. Previous studies have examined the effect of scraping and flushing manure on ammonia emissions from fresh manure alone. This study, however, focuses on handling effects on ammonia emissions from the dairy operation as a whole, including the barn floor, holding tanks, separated solids stockpiles, and separated liquid storage, and thus is able to identify the stage of handling with the greatest potential to control emissions. Four stages of manure handling were examined:

1. Scrape - Fresh mixture of urine and feces to represent what may be *scraped* from a barn floor
2. Flush - Diluted mixture of urine and feces to represent what is *flushed* from a barn floor
3. Separated Solids – What was *retained* in a solids separator following separation of a diluted mixture of urine and feces
4. Separated Liquid – *Permeate* from a solids separator following separation of a diluted mixture of urine and feces

The second objective of this study is to determine the effects of dietary protein manipulation on ammonia fluxes from relatively fresh cattle manure slurries. Cows were fed diets formulated to vary in crude protein content from 14.5 to 18%. The majority of previous studies on dietary protein manipulation have concentrated on emissions from one aspect of a dairy operation, usually the feeding operation. Our research, however, focuses on the effect of dietary protein manipulation on emissions from the entire manure handling operation at a flush dairy.

3.3 Methods

Facility

This study was conducted at the Virginia Tech Dairy in Blacksburg, Virginia. The Virginia Tech Dairy has a free-stall barn that employs a flushing system, to clean the barn floors of manure. The barn floor is flushed four times a day with recycled effluent from a manure storage tank . The effluent, a combination of flush water and fresh urine and feces, flows to a temporary holding tank, where it is held for approximately 24 hr. From the holding tank, the manure is delivered to a solids separator. Permeate from the solids separator is sent to the storage tanks, while separated solids are stockpiled for subsequent use as fertilizer.

Experiments ran from the spring of 2006 to the spring of 2007. Seven Holstein cows were fed four diets formulated to contain dietary protein contents of 14.5, 15.5, 17, and 18%. Forage levels in all diets were fixed at 50% of diet dry matter and composed of 80% corn silage, 6% alfalfa hay, and 14% grass hay. The grain mix represented the remaining 50% of the diet and was manipulated using a combination of corn, soyhulls, soybean meal, ruminally protected soybean meal, and tallow to achieve the targeted CP densities while maintaining constant dietary energy levels.

Each feeding period consisted of a 14-day diet acclimation period, followed by a 5-day manure collection period. During the acclimation periods, cows were housed in a free-stall barn. For the manure collection period, we moved cows to individual stalls in a smaller adjacent barn. Based on changes made halfway through this project in the methods employed for manure collection and ammonia gas analysis, this methods section is henceforth separated into two subsections: Summary of Study 1 and Summary of Study 2 (Table 3.1).

Summary of Study 1

The protocol for manure collection and handling was designed to mimic methods used in previous studies and to facilitate collection and laboratory analysis. The cows' stalls had a slatted floor, and we placed a tray beneath the slats to catch feces. We manually collected feces lodged in the slats or on the stall floor and added them to the tray. Every 24 hr, we transferred feces from the trays to plastic 35-gal drums (BRUTE Rubbermaid) for weighing.

We mixed the feces in each drum with a heavy-duty drill and paddle bit. We collected ~500-g sub-samples of feces from each drum for total Kjeldahl nitrogen (TKN) analysis using Ziploc bags. We sealed the Ziploc bags and froze them until the TKN analysis. Following feces collection, we sealed the drums with lids and placed them in a freezer until further testing. Freezing manure prior to ammonia analyses is commonly practiced, and there is no evidence that freezing affects the results [31, 33]. Additionally, freezing the manure is perhaps the best way to suppress ammonia loss during manure storage.

We collected urine by catheterizing each cow. The ends of the catheters were placed in 5-gal jugs. Every 24 hr, at the same time feces were collected, we collected urine jugs and weighed them. Using plastic vials, we collected 50-mL sub-samples of the urine for TKN analysis. We acidified and capped the sub-samples and placed them in a freezer until the TKN analysis. Following sampling, we sealed the jugs with screw-on caps and placed them in a freezer until further testing.

Two to four days before testing, we removed the urine and feces from the freezer to thaw. When urine and feces were thawing, they remained covered and separate. Urine and feces usually thawed by exposure to ambient temperatures. However, during the colder months, we placed the containers in hot water baths to accelerate the process.

Preparation for Scraped Manure Ammonia Analyses

We placed 25% of thawed feces that were collected from one 24-hr period in an ~80-L test-tub, the bottom quarter of a 35-gal drum (BRUTE Rubbermaid). After adding feces to the test-tub, we mixed thawed urine manually and added it to the feces. We used 25% of the urine excreted over the same 24-hr period as the feces. We mixed urine and feces manually and moderately using a paddle.

We sub-sampled ~200 mL of the slurry from the test-tub into a 250-mL bottle for TKN analysis. We acidified the sub-sample, sealed it, and stored it at 4^{o}C until the TKN analysis.

Preparation for Flushed Manure Ammonia Analyses

To generate a flushed manure sample, we followed the same procedure that we used to generate a scraped manure sample. However, we transferred the urine and feces to another 35-gal drum before adding them to the test-tub. We added fresh water to the urine and feces in the drum at a *water weight-to-manure weight* proportion of *4-to-1*. We mixed this slurry and transferred ~18 kg of the mixed slurry from the drum to the test-tub using a bucket. As with the scraped manure, we sub-sampled a portion of the slurry from the test-tub for TKN analysis.

Preparation for Separated Solids/Liquid Ammonia Analyses

To generate a separated liquid/solids manure sample, we began by preparing a flushed sample in an empty 35-gal drum, except we used 50% of the urine and feces excreted over the same 24-hour period in order to obtain more solids from the separation. We covered the drum and allowed the sample to sit idle for approximately 24 hr to simulate the storage period prior to separation. After the storage period, we used a pilot-scale solids separator to separate the solids from the liquid in the flushed sample. Separated liquid was collected in 19-L buckets, and

separated solids were collected in a tray. We sub-sampled a portion of the slurry/solids from the test-tub for TKN analysis as we did for the scraped and flushed manure.

Ammonia Flux Measurements

We constructed a dynamic flux chamber based on an EPA-approved design to measure ammonia emitted from the manure [40]. The clear acrylic chamber is cylindrical with a domed top and has a volume of 49 L. It uses a sweep-air flow rate of 7 L min^{-1}, the same as in previous studies with a chamber of similar dimensions [41, 42]. We used ambient air at the dairy as our sweep-air source. Its ammonia concentration averaged 0.310 mg m^{-3}, which was at least two orders of magnitude lower than the concentrations typically measured during the manure analyses. To achieve well-mixed conditions, we pumped sweep-air through the chamber for ~30 min (3.5 residence times) before each test [45]. The duration of flux measurements for each test varied between 14 hr and 4 d.

Temperature and ammonia concentrations in the outlet from the chamber's headspace were measured using a photoacoustic infrared (IR) analyzer (INNOVA Air Tech 1312) and temperature/relative humidity data loggers (HOBO), respectively. We programmed the photoacoustic analyzer to sample at intervals varying between twice a minute and once every five minutes. The instrument has a detection limit of 1.4×10^{-7} mg m^{-3} and was calibrated (California Analytical, Orange, CA) one month prior to the study. Test durations were on the order of 24 hr.

We validated the flux chamber by comparing loss of ammonium from a known volume of solution placed in the chamber to the gaseous flux leaving measured by two methods: diffusion denuders and the photoacoustic analyzer. The two methods agreed well, and recovery fractions were not significantly different from 100%.

Summary of Study 2

The purpose of the second study was to repeat the experiments in Study 1 but to remove temperature as a variable by conducting all experiments at 15.6°C rather than variable ambient conditions. We tried to control the temperature of manure in the second study so that diet and handling effects on ammonia flux could be distinguished from temperature effects.

The diets, housing of the cows, and collection of manure were the same as in Study 1. We thawed the manure and conducted flux measurements in a room that is moderately temperature-controlled at the Virginia Tech Dairy. It can be easily maintained at approximately 15.6°C in the winter using thermostatically controlled wall heaters and in the spring purely by its well-insulated walls and lack of sunlight penetration. We kept the temperature of the manure constant by placing thermostatically controlled BriskHeat drum heaters and insulation around the test-tubs. We also replaced the Teflon tubing used for sweep-air distribution with more thermally conductive copper tubing. We placed thermostatically controlled heating tape and pipe insulation on the copper tubing.

Prior to sub-sampling a portion of the slurry for TKN analysis before each flux measurement, we mixed the slurry more intensely than in Study 1 using egg-beaters. Study also differed in that we determined total ammoniacal nitrogen (TAN), in addition to TKN, of each manure sample. In Study 1, the urine-to-feces ratio averaged 0.495±0.040 by mass. In Study 2, we kept this ratio constant.

Table 3.1: Variables in each test of ammonia flux

Test[a]	%CP	Mixing Intensity	Temperature Control	U/F[b]
1	18	low	N	0.38
2	15.5	low	N	0.43
3	14.5	low	N	0.42
4	18	low	N	0.61
5	17	low	N	0.51
6	18	low	N	0.67
7	17	low	N	0.52
8	14.5	low	N	0.52
9	18	high	Y	0.50
10	15.5	high	Y	0.50
11	14.5	high	Y	0.51
12	17	high	Y	0.50
13	15.5	high	Y	0.46
14	14.5	high	Y	0.50
15	17	high	Y	0.50
16	15.5	high	Y	0.50
17	14.5	high	Y	0.50
18	18	high	Y	0.50
19	17	high	Y	0.50
20	14.5	high	Y	0.50

[a]Each test consisted of four types of manure: scrape, flush, separated solids and liquid manure
[b]Average of the urine-to-feces ratios from each type of manure in a test

Table 3.1 summarizes the conditions of each test, where a single test represents manure from a single cow fed a diet containing a specific amount of crude protein. Tests 1-8 comprise Study 1, and Tests 9-20 comprise Study 2.

Temperature Corrections and Statistical Analyses

Because ammonia fluxes are extremely sensitive to temperature, we found it necessary to correct our results for temperature not only in Study 1, but also in Study 2, in which we controlled temperature to a narrower range. Temperature corrections were necessary to allow us to distinguish diet effects from temperature effects and also allowed us to combine data from both studies into one analysis.

We compared results on the basis of mass of ammonia lost over a constant time period of 18 hr ($Mass_{0\text{-}18hr}$). For the scraped and flushed manure, the period of interest was the 18 hr immediately following mixing of urine, feces, and in the case of flushed manure, fresh water. For the separated solids and liquid manure, it was the 18 hr following separation, i.e. the 18 hr following the 24 hr storage period. We corrected $Mass_{0\text{-}18hr}$ to 15°C according to the van't Hoff equation, which describes the temperature dependence of Henry's constant:

$$K_{H\text{-}2} = K_{H\text{-}1} \times e^{\left[{}^{\Delta H}/_{R} \times \left({}^{1}/_{T_1} - {}^{1}/_{T_2}\right)\right]}$$

Equation 3.2: van't Hoff equation

Where: $K_{H\text{-}2}$ = Henry's constant at T_2
T_2 = temperature, K
$K_{H\text{-}1}$ = Henry's constant at T_1
T_1 = temperature, K
ΔH = enthalpy of solution for ammonia, -8.17 kcal mol^{-1}
R = ideal gas constant, 0.001987 kcal K^{-1} mol^{-1}

Assuming K_H is proportional to the gaseous ammonia concentration and the mass of ammonia lost, the van't Hoff equation is rearranged to determine $Mass_{0\text{-}18hr}$ corrected to 15°C:

$$Mass_{0\text{-}18hr(Corr.)} = Mass_{0\text{-}18hr(Meas.)} \times e^{\left({}^{4112}/_{T_{Meas.}} - 14.28\right)}$$

Equation 3.3: Adjusted van't Hoff equation

Where: $Mass_{0\text{-}18hr(Corr.)}$ = mass of ammonia lost during the first 18 hr corrected to 15°C, mg *N*
$Mass_{0\text{-}18hr(Meas.)}$ = measured mass of ammonia lost during the first 18 hr, mg *N*
$T_{Meas.}$ = measured average temperature during the first 18 hr, K

Data analysis focused on addressing the following four questions: (1) In each stage of handling, does the majority of ammonia volatilize from manure during the first half or second half of the period of interest (18 hours)? (2) Do ammonia emissions from freshly excreted manure vary with mixing intensity of the urine and feces? (3) In each stage of manure handling,

how do ammonia emissions vary with crude protein intake? (4) How well do TKN, TAN, and temperature predict ammonia emissions in each stage of manure handling? Table 3.2 lists the analysis performed or parameter of interest calculated for each question. It also shows the data used, temperature correction applied, and tables and figures related to each case. We excluded outliers whose standardized residuals were greater than a factor of two from each analysis when the outliers could be explained by extreme temperatures.

Table 3.2: Methods used to analyze results

Purpose	Statistical Analysis/Parameter of Interest	Data Grouping	Temperature Correction	Relevant Figures/Tables
To quantify when during the period of interest the majority of ammonia volatilizes from each type of manure	The ratio of the temperature-corrected mass of ammonia lost in the second 9 hr to the mass lost in the first 9 hr during the period of interest $(\frac{Mass_{9\text{-}18hr}}{Mass_{0\text{-}9hr}})$	Data from all seven cows was grouped according to type of manure	The mass lost during the first 9 hr and the mass lost during the second 9 hr were both corrected to 15°C using the adjusted van't Hoff equation	Table 3.3
To determine an average mass lost during the period of interest for each type of manure ($Mass_{0\text{-}18hr}$)	Average $Mass_{0\text{-}18hr}$ values for each type of manure	Data from all seven cows was grouped according to manure type	$Mass_{0\text{-}18hr}$ values were corrected to 15°C using the adjusted van't Hoff equation	Table 3.3
To determine the effect of mixing intensity on ammonia emissions from freshly excreted manure	t-test using Minitab statistical software Hypothesis: $\mu_2 - \mu_1 > 0$ Sample 1: $Mass_{0\text{-}18hr}$ values from Study 1 (moderate mixing intensity) Sample 2: $Mass_{0\text{-}18hr}$ values from Study 2 (high mixing intensity)	Only data from the scraped manure was used in this analysis	$Mass_{0\text{-}18hr}$ values were corrected to 15°C to remove temperature as a variable, thereby isolating mixing intensity as the sole difference between the two sample sets	N/A
To determine the effect of crude protein intake on ammonia emissions from each type of manure	Simple regression using Minitab statistical software Predictor variable: Crude protein intake Response: $Mass_{0\text{-}18hr}$	Data from all seven cows was grouped according to type of manure	$Mass_{0\text{-}18hr}$ values were corrected to 15°C to remove temperature as a variable, thereby isolating crude protein intake as the sole predictor of ammonia volatilization	Figure 3.5 Figure 3.6 Figure 3.7 Figure 3.8

Purpose	Statistical Analysis/Parameter of Interest	Data Grouping	Temperature Correction	Relevant Figures/Tables
To determine the effect of dietary crude protein content on the excreted mass of TKN in the urine and feces of each cow	Paired t-test using Minitab statistical software Hypothesis: Sample 2 > Sample 1 Sample 1: Average mass of excreted TKN for the two lower protein diets Sample 2: Average mass of excreted TKN for the two higher protein diets	For each cow, the average mass of excreted TKN for the two lower protein diets was paired against the average mass of excreted TKN for the two higher protein diets	None	Figure 3.9
To determine the effect of TKN alone, T alone, TAN alone, TKN and T together, and TAN and T together on the mass of ammonia lost during the period of interest	Multivariable regression using Minitab statistical software Predictor variables: TKN, TAN, and T Response: Mass of ammonia lost during the period of interest ($Mass_{0\text{-}18hr}$)	Data from all seven cows was grouped according to manure type	None, temperature is included as a predictor variable in the regression	Table 3.4

3.4 Results and Discussion

Temperature and pH Effects

In the scraped and flushed manure, fluxes rose steadily from zero during the first 3-50 hr (average of 25 hr) and afterward were closely correlated with ambient temperatures (Figure 3.1 and Figure 3.2). In contrast, previous studies involving cattle urine and slurries applied as fertilizer found an immediate burst of flux that tapered off [22, 23]. We hypothesize that urea hydrolysis was rapid upon urine application to feces, but that a relatively low initial pH prevented high initial fluxes because most of the TAN was present as ammonium and not free ammonia. pH values averaged 6.87±0.17 and 7.05±0.13 in the scraped and flushed manure,

respectively (Table 3.3). Only after the pH rose to average values of 8.56±0.09 and 8.58±0.09 at the end of the analyses in the scraped and flushed manure, respectively, had ammonia fluxes reached a maximum (Table 3.3).

These results are consistent with the pH-controlled mechanism for ammonia flux proposed by Ni et al. [17]. Dissolved carbon dioxide naturally contained within manure and that formed from the breakdown of carbonic acid are released, causing the pH to rise and facilitating the conversion of ammonium to aqueous ammonia and ultimately ammonia gas, as observed in other studies [18]. Essentially, in our tests, the pH values of the scraped and flushed manure slurries were initially unfavorable to ammonia mass transfer to the gaseous phase. However, as the slurries aged and the pH rose due to the release of carbon dioxide, the ammonia flux peaked and then became controlled by temperature (Figure 3.1 and Figure 3.2).

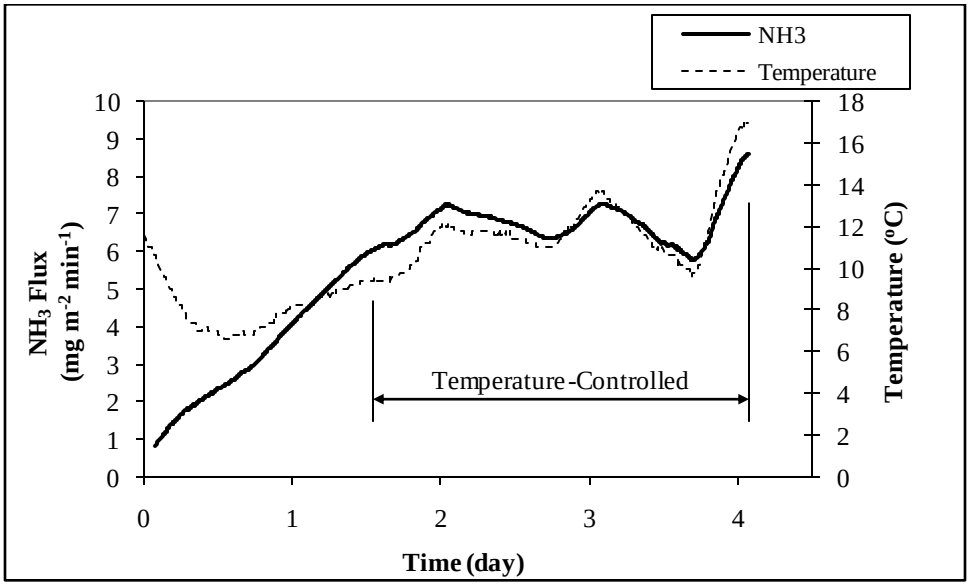

Figure 3.1: Ammonia flux and temperature from the scraped manure with the temperature-controlled region highlighted

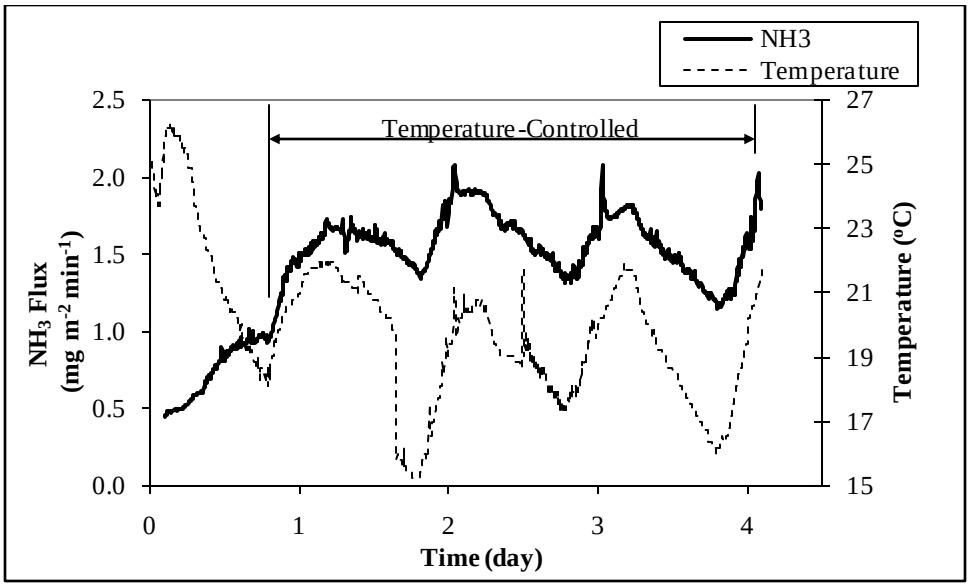

Figure 3.2: Ammonia flux and temperature from the flushed manure with the temperature-controlled region highlighted

For tests with the separated solids and liquid manure, fluxes did not gradually rise over several hours but rather tracked with temperature from the beginning (Figure 3.3 and Figure 3.4). The temporal pattern of flux was similar to that reported in the literature for cattle urine applied to soil and aged cattle slurries applied as fertilizer [21-23]. Immediately after the manure was prepared, the pH was already favorable to ammonia mass transfer to the gaseous phase, so pH was not a controlling factor for emissions. In the separated solids and liquid manure, initial pH values averaged 8.70±0.30 and 8.55±0.19, respectively, and were similar to the pH values at the end of the test, 8.89±0.20 and 8.51±0.19, respectively (Table 3.3). The strong correlation with temperature stems from the temperature dependence of Henry's law, i.e. partitioning toward the gaseous versus aqueous phase is favored at higher temperatures. It is likely that pH increased during the 24-hr storage period of the manure prior to separation; the separated solids and liquid manure may be classified as aged slurries.

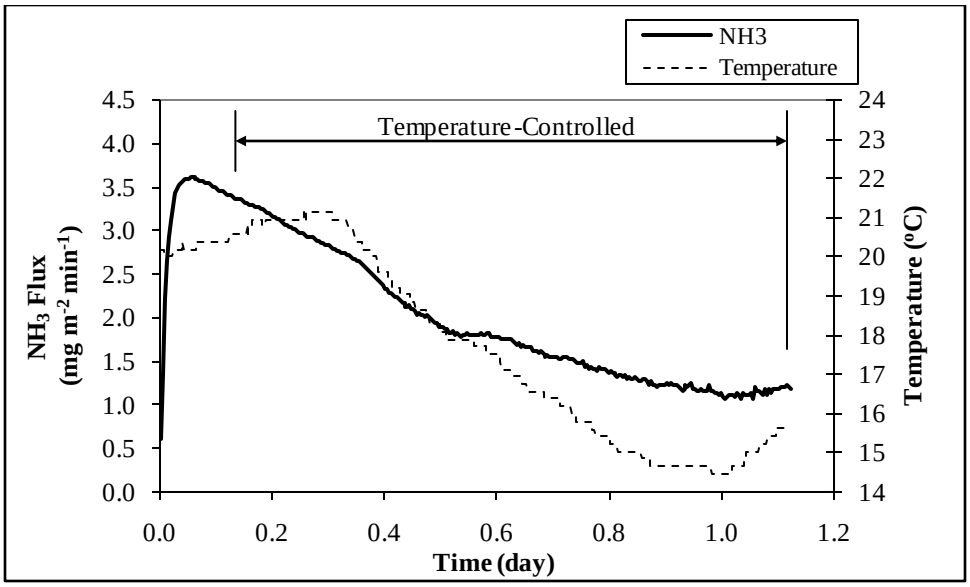

Figure 3.3: Ammonia flux and temperature from the separated solids manure with the temperature-controlled region highlighted

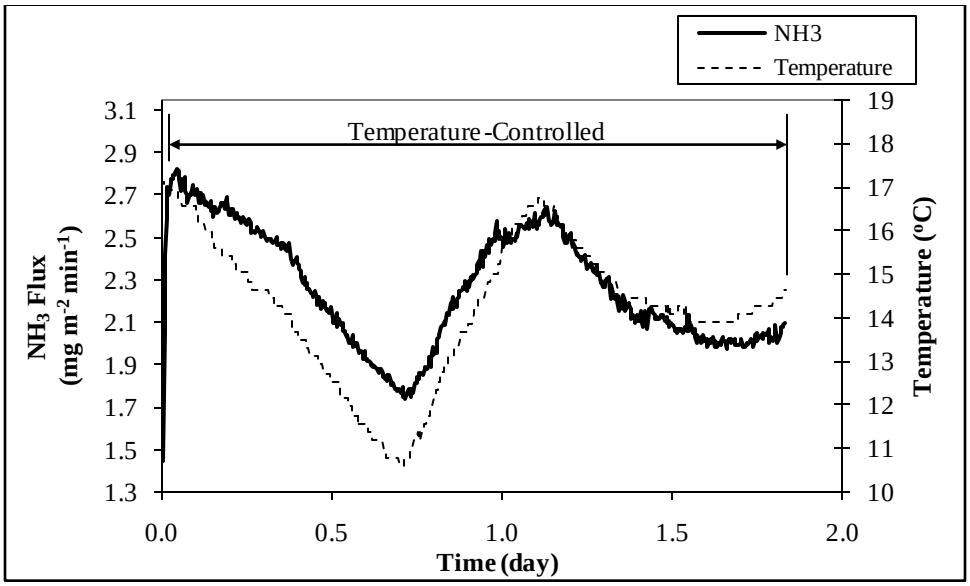

Figure 3.4: Ammonia flux and temperature from the separated liquid manure with the temperature-controlled region highlighted

Manure Handling Effects

The four different manure handling methods yielded different temporal patterns and magnitudes of ammonia fluxes. As described above, ammonia emissions from the scrape and flush manure rose slowly from zero over the course of several hours and then tracked

fluctuations in temperature. In contrast, ammonia emissions from the separated solids and liquids were relatively high and temperature-controlled from the start. Over the period of interest, the highest amount of ammonia lost came from the scrape manure (Table 3.3).

We quantified differences in ammonia emissions between the scrape and flush manure and between the separated solids and liquid manure. In comparing results from different types of manure, we isolated subsets of measurements from the same cow and the same diet to eliminate cow-to-cow variability and dietary effects. We also controlled for temperature by correcting all estimates of ammonia lost to 15°C using the adjusted van't Hoff equation.

The magnitude of fluxes varied considerably between the scrape and flush manure. The mass of ammonia emitted from the scrape manure exceeded the mass emitted from the flush manure by a factor of 4.61±2.03 (ignoring dietary effects). These results are consistent with the 1:5 dilution of the urine-feces mixtures to create flush manure.

Table 3.3 shows the ratio of the temperature-corrected mass of ammonia lost in the second 9 hr to the mass lost in the first 9 hr during the period of interest ($\frac{\text{Mass}_{9\text{-}18\text{hr}}}{\text{Mass}_{0\text{-}9\text{hr}}}$). We used this parameter to quantify when the majority of the ammonia mass was lost during the period of interest, whether during the first half, in which case the ratio would be less than one, or the second, in which case the ratio would be greater than one. The scrape and flush manure had ratios of ~2, which emphasizes the slow rise in emissions during the first half of the 18-hr period. The separated solids and liquids had ratios close to 1, meaning that approximately equal amounts of ammonia were lost during the first and second halves of the period of interest.

The initial TAN/TKN ratio ($\frac{\text{TAN}_0}{\text{TKN}_0}$) differed substantially between the scrape and flush manure. Our hypothesis that the rate of urea hydrolysis was initially high in the scrape manure

was confirmed by the relatively high $\frac{TAN_0}{TKN_0}$ ratio of 49.7±14.3%, compared to 5.02±1.05% in the flush manure (Table 3.3). Because the urine, feces, and fresh water were mixed simultaneously, urea concentrations in the flush manure should be lower, yielding lower initial rates of hydrolysis.

While in the separated liquid, fluxes remained relatively constant with temperature as the test progressed, in the separated solids, fluxes gradually decreased over time, as shown in Figure 3.3 and Figure 3.4 and by the average $\frac{Mass_{9\text{-}18hr}}{Mass_{0\text{-}9hr}}$ values for each type of manure. The $\frac{Mass_{9\text{-}18hr}}{Mass_{0\text{-}9hr}}$ values were 0.89±0.16 and 1.12±0.22 in the separated solids and liquid, respectively (Table 3.3). This indicates that, on average, 11% less mass was lost during the second 9 hr than during the first 9 hr in the separated solids, while equal masses were lost during each period in the separated liquid. This suggests that aqueous ammonia limitation begins earlier in the separated solids than in the separated liquid.

Table 3.3: Summary of initial and final pH, initial TAN/TKN ratio, timing of ammonia volatilization, and total mass of ammonia lost over the period of interest by manure type corrected to 15°C (average±standard deviation)

Manure	pH_0	pH_f	$\frac{TAN_0}{TKN_0}$	$\frac{Mass_{9\text{-}18hr}}{Mass_{0\text{-}9hr}}$	$Mass_{0\text{-}18hr}$
Scrape	6.87±0.17	8.56±0.09	0.497±0.143	2.21±0.56	760±463
Flush	7.05±0.13	8.58±0.09	0.050±0.010	2.34±0.47	172±76
Sep. Solids	8.70±0.30	8.89±0.20	0.253±0.055	0.89±0.16	428±157
Sep. Liquid	8.55±0.19	8.51±0.19	0.443±0.102	1.12±0.22	437±158

A t-test using the masses lost from scrape manure following mixing with moderate intensity versus high intensity shows that raising mixing intensity increases ammonia fluxes by a margin significantly greater than zero (M=115%, p=0.002, 95% C.I. = 43, 188%). Therefore, efforts to minimize mixing of fresh manure may help reduce emissions from a feeding lot.

One limitation of this study is that the flush manure we generated in the laboratory, in which fresh manure is immediately diluted, emulates situations when manure is excreted onto a barn floor and then immediately flushed. In reality, manure may sit on the barn floor for many hours before being diluted, in which case results from our scrape manure are more applicable. However, results from our flush manure will also apply to flushed manure that is stored in open-air holding tanks before further processing of the manure.

Dietary Effects

Figure 3.5, Figure 3.6, Figure 3.7, and Figure 3.8 show the mass of ammonia lost versus crude protein intake per day in each type of manure. The figures include results from all seven cows corrected to 15°C. Each point in the figures corresponds to the mass of ammonia lost over the period interest from a manure sample collected from one cow, following a feeding period with one of the four diets. More specifically, each point corresponds to one row in Table 3.1.

None of the least-squares linear regression slopes are significant in any of the four types of manure. Crude protein intake alone may serve as a poor predictor in all manure types due to the cow-to-cow variability. For any specific cow, there is a general trend of greater ammonia loss with higher levels of crude protein intake in the separated solids and liquid manure.

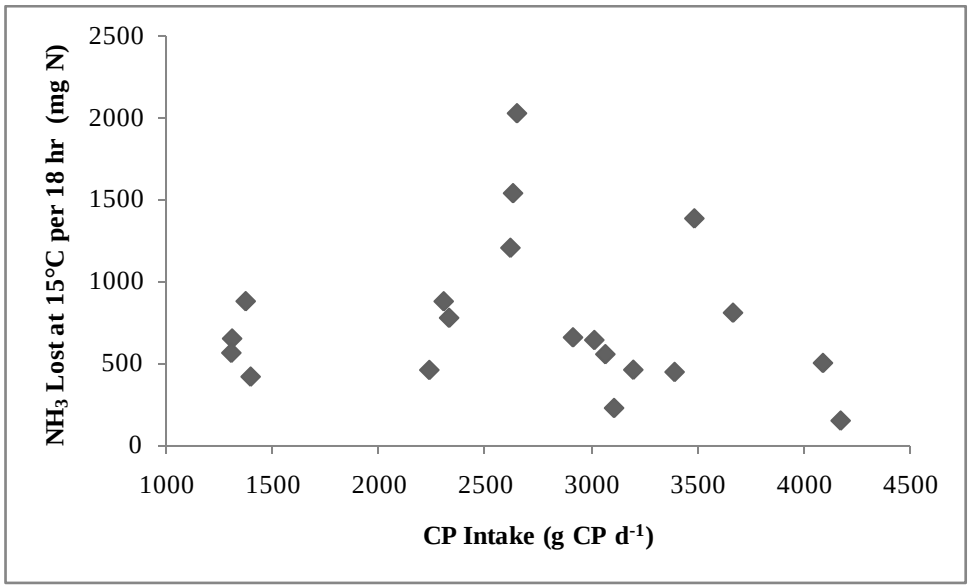

Figure 3.5: Ammonia lost per 18 hr as a function of crude protein intake in the scrape manure

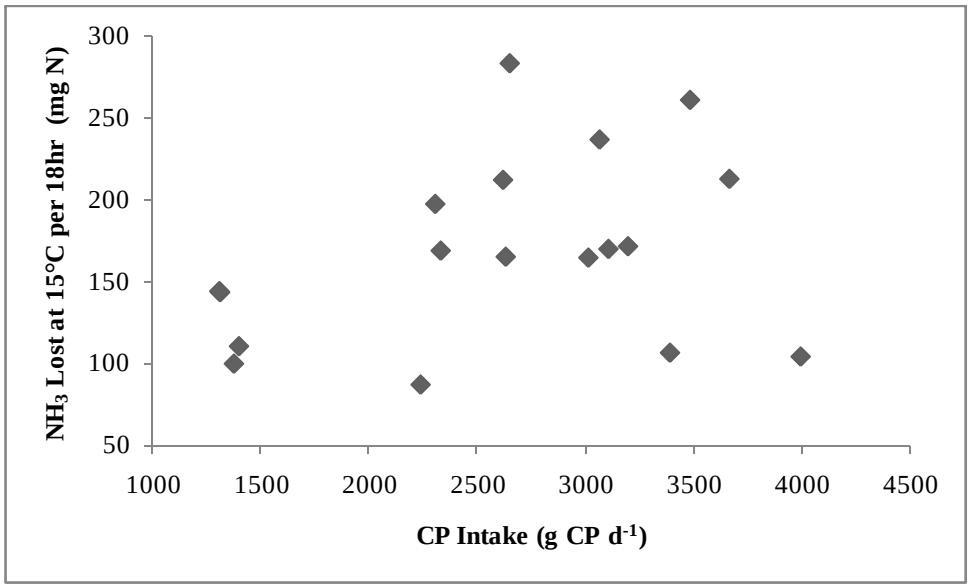

Figure 3.6: Ammonia lost per 18 hr as a function of crude protein intake in the flush manure

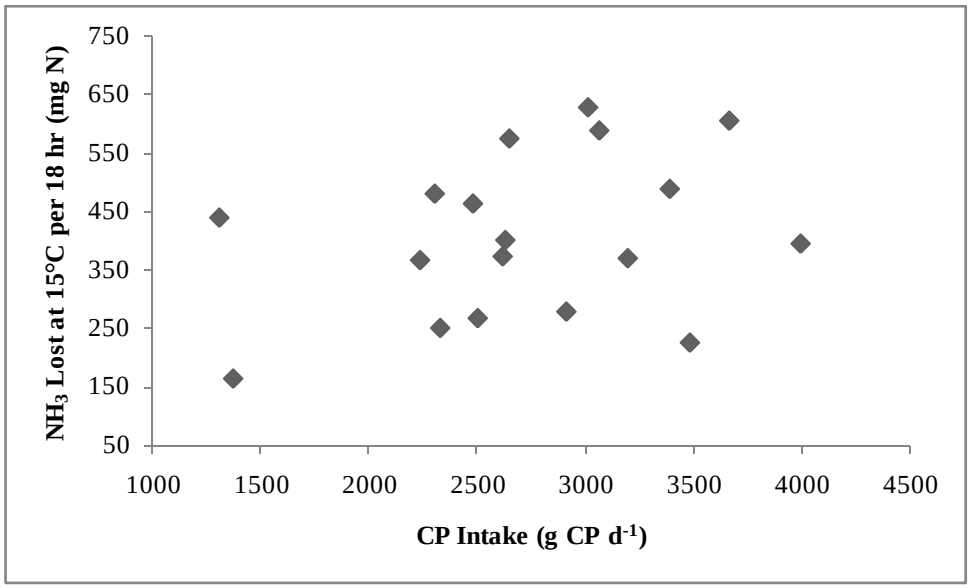

Figure 3.7: Ammonia lost per 18 hr as a function of crude protein intake in the separated solids manure

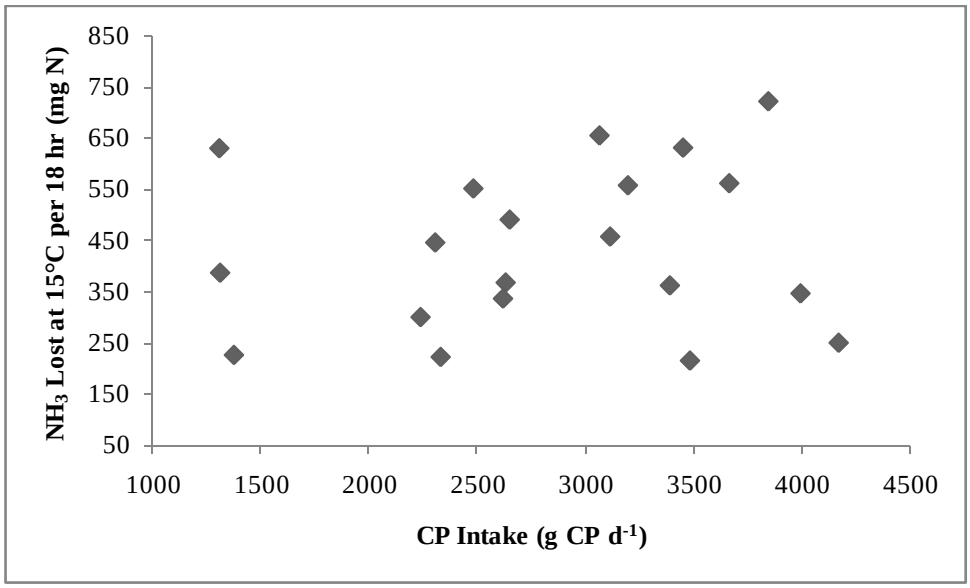

Figure 3.8: Ammonia lost per 18 hr as a function of crude protein intake in the separated liquid manure

Synthesis

This section links the results shown previously to demonstrate that a reduction in dietary protein content has the potential to reduce ammonia emissions from dairy cattle operations. Mechanistically, a reduction in dietary protein could correspond to a reduction in excreted

nitrogen (TKN and TAN). If at least some of the TAN is present as ammonia rather than ammonium, then some of it will volatilize under typical environmental conditions. Therefore, a reduction in dietary protein content should result in a reduction in ammonia emissions.

Figure 3.9 shows that lowering dietary protein resulted in a reduction in protein intake and in the average excreted mass of TKN. For each cow, we grouped data from the two higher protein diets and the two lower protein diets and performed a paired t-test on the excreted masses of TKN. Reducing crude protein resulted in a reduction in the excreted mass of TKN significantly greater than zero (M=11%, p=0.063, 95% C.I. = 0, 23%).

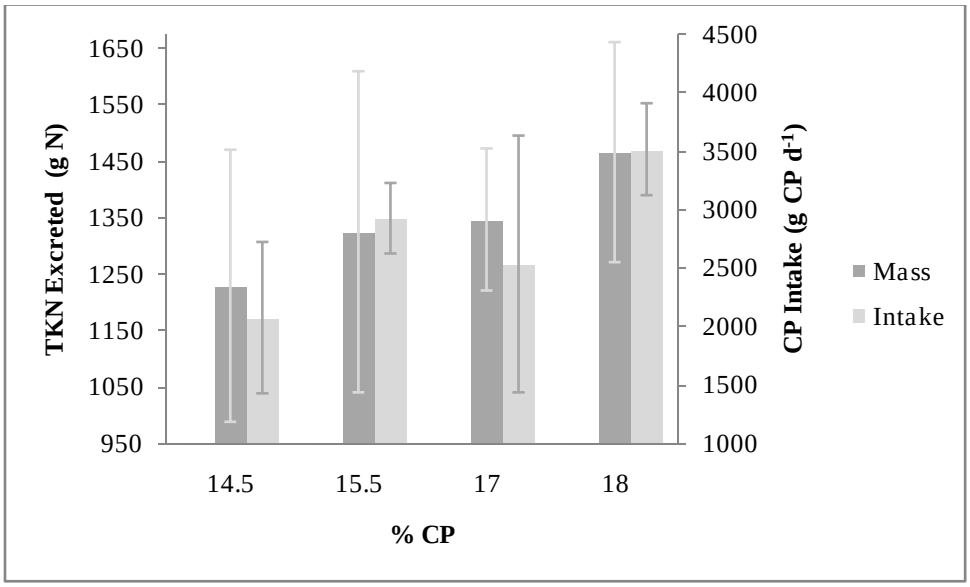

Figure 3.9: Average mass of TKN excreted and average intake per diet for the seven cows used in this study

Table 3.4 displays correlation coefficients derived from regressions used to establish relationships between $Mass_{0\text{-}18hr}$ and T alone and T together with TKN or TAN. Monteny et al. [16] showed that the $\log_{10}$ of the gaseous ammonia concentration varies linearly with temperature for ammonia emissions from a dairy cow house. Based on this result and the linear

relationship between ammonia fluxes and TKN/TAN as is suggested by Henry's law, T and log(TKN) or log(TAN) were used to predict log($Mass_{0\text{-}18hr}$) in the multivariable regression.

The mass of ammonia lost is correlated with both TKN and TAN. The higher R^2 values for TAN in the scrape, separated solids, and separated liquid manure indicate that it is a better predictor for ammonia flux than is TKN, as we would expect given that TAN is a more direct measure of aqueous ammonia in solution. It is important to note that T alone is a strong predictor of ammonia fluxes in the scrape and flush manure, indicating that T is the controlling factor in ammonia loss from those particular stages of manure handling. Adding TKN or TAN as predictor variables only slightly improves the R^2 values. These results suggest that the temperature effects on ammonia flux may overshadow any effects of dietary protein manipulation in the scrape and flush manure. The relationships for the separated solids and separated liquid manure are very similar to that derived by Monteny et al. [16] ($10^{-9.71} \times 1.05^{T} \times$ TAN).

Comparison of the nitrogen volatilized as ammonia versus the change in nitrogen concentration in the manure slurry, i.e. a nitrogen mass balance, was limited by uncertainties in the TKN analysis. The change in TKN in the manure over the duration of the test was relatively small, so the calculated mass of nitrogen lost during the test was highly uncertain. These uncertainties precluded calculation of a meaningful mass balance.

Table 3.4: Coefficient of determination of multiple regressions between log($Mass_{0\text{-}18hr}$) and T alone, T & TKN, and T & TAN as a function of manure type; and equations for the T & TAN regressions

Manure	R^2			Model parameters for each term with T and log(TAN) as predictor variables for log($Mass_{0\text{-}18hr}$)			$Mass_{0\text{-}18hr}$ as a function of T and TAN[a]
	T (K)	T & TKN (mg N L^{-1})	T & TAN (mg N L^{-1})	log(TAN) (*p*-value)	T (*p*-value)	Constant (*p*-value)	
Scrape	0.727	0.601	0.761	0.176±0.155 (0.284)	0.073±0.016 (0.001)	-18.2±4.4 (0.002)	$10^{-18.2} \times 1.18^{T} \times TAN^{0.176}$
Flush	0.561	0.723	0.666	0.475±0.283 (0.127)	0.082±0.023 (0.006)	-22.5±6.6 (0.008)	$10^{-22.5} \times 1.21^{T} \times TAN^{0.475}$
Sep. Solids	0.289	0.472	0.906	1.34±0.185 (0.000)	0.025±0.007 (0.009)	-8.24±2.04 (0.004)	$10^{-8.24} \times 1.06^{T} \times TAN^{1.34}$
Sep. Liquid	0.360	0.445	0.812	0.882±0.190 (0.001)	0.032±0.011 (0.018)	-9.15±3.13 (0.017)	$10^{-9.15} \times 1.08^{T} \times TAN^{0.882}$

[a] $Mass_{0\text{-}18hr} = 10\text{^}\log(Mass_{0\text{-}18hr})$

3.5 Conclusions

The results from this study have shown that a reduction in protein intake may lead to a reduction in excreted TAN in the manure and that ammonia fluxes in the separated solids and liquid manure are well correlated with TAN. The combination of temperature and TAN are strong predictors of the amount of ammonia lost over the first 18 hr in the separated solids and liquid manure.

The operating procedures of an individual dairy will play a critical role in determining what stage of handling contributes the majority of ammonia to the atmosphere. The results from this study suggest that there are strategies that can be incorporated into a dairy's manure handling operation to drastically reduce ammonia emissions.

Despite the positive correlation between mixing intensity and emissions, some mixing between bovine urine and feces is desired to maintain lower pH values that favor ammonium over ammonia in solution. If cattle urine is excreted onto a feces patch without penetration or onto a barn floor contaminated with urease, a urine-on-soil scenario is created. In this case, urease is allowed to hydrolyze urea by diffusion and the caustic pH (7.95±0.36) of the urine is retained, allowing for a high degree of ammonia volatilization and an immediate burst in ammonia flux. Since feces are typically excreted at a larger proportion in terms of mass, dairies must encourage mixing between excreted urine and feces, and use the natural acidity of the feces (6.11±0.40) to lower the pH of the slurry and delay ammonia volatilization as was done in this study. If a dairy can promote the development of well-mixed slurries on the barn floor and flush at least four times per day, it can successfully delay ammonia volatilization to another stage of handling in which it would have more control over emissions. It should be noted that dairies

would need to determine the proper balance between no mixing and high intensity mixing to minimize emissions. Given that pig houses utilizing urine/feces separation systems have been shown to reduce ammonia emissions, encouraging mixing may be a method for reducing ammonia emissions that is only applicable to dairies with solid floors.

Covering holding tanks prior to solids separation will minimize carbon dioxide stripping and prevent the pH from rising to levels favorable to ammonia mass transfer to the gaseous phase. In this study, slurry pH values reached 8.56±0.09 and 8.58±0.09 in the scrape and flush manure, respectively, after sitting idle for a day. At the holding tank discharge, adding enough alkalinity to the slurry to allow for nitrification in the storage tanks will result in biological conversion of ammonia to nitrate, a strategy recommended by the EPA to reduce ammonia emissions [52]. One study showed the optimal pH range for nitrification of dairy waste is between 7.0 and 7.2, as higher pH values typically result in free ammonia inhibition [53]. In the process of nitrification, ammonia emissions will be kept at a minimum in this pH range.

Nitrification is not currently required at flush dairies; however, wastewater treatment regulations will only become more stringent as long as nutrient levels in agricultural runoff continue to deteriorate water quality in receiving estuaries, such as the Chesapeake Bay. Future regulations may require only nitrification or nitrification and denitrification. The combination of these biological conversion processes would convert ammonia to harmless nitrogen gas. Such regulations would be burdensome to dairies, as supplying enough air and alkalinity for nitrification will present a significant operating cost. Additionally, the combination of nitrification and denitrification would reduce the amount of usable fertilizer produced by dairies.

4 Appendices

4.1 Appendix A - Methods Used for Manure Gas Analyses Taken from Literature

Ref.	Methods Used for Manure Gas Analyses
[30, 31]	Relatively small polyethylene chambers (20 cm × 20 cm × 12 cm deep) were used to contain ammonia gas emitted from slurries applied to soil. Vacuum pumps were used to pull ammonia gas from the chamber through acid traps containing 100 mL of 0.90 M sulfuric acid. Ammonia was collected for seven days following slurry application to the soil. TAN in the acid traps was determined colorimetrically.
[32]	Manure samples were collected in 50-g quantities. Air was drawn over the manure samples in a flask at a flow rate of 0.80 L min^{-1}. Ammonia laden air was then introduced into 100 mL of 0.1 M sulfuric acid. Ammonia from the acid traps was determined by distillation.
[33]	Slurries consisted of 5 g of feces and 3.9 mL of urine in a 250-mL Nalgene bottle. Air from the headspace of the bottle was drawn into two boric acid traps at a flow rate of 0.5 to 1.5 L min^{-1} and test lengths varied between 2 and 12 hours.
[34]	A 2.5 m-tall instrument mast was placed in the center of an artificial feedyard surface housing acid traps at various heights above the surface. Acid traps contained 0.05 M sulfuric acid. Flow rate through the traps was approximately 6 L min^{-1}. A flow-injected-analyzer was used to quantify ammonia trapped in the acid.
[35, 36]	Chambers employing a ventilation rate of 100 m^3 m^{-2} h^{-1} were used to contain ammonia gas from manure samples. Ammonia gas was quantified using reagent tubes. Manure samples were comprised of a portion of manure excreted over a 4-day period on a stall floor.
[38]	Ventilation air in a cubicle-house collected ammonia gas emitted from slurries on the stall floor. Ventilation air was exhausted to a heating apparatus, converting NH_3 to NO. Exhaust air was then measured for NO_x using a NO_x analyzer.
[39]	Wind tunnels collected ammonia gas emitted from soil patches and delivered it to acid traps containing 80 mL of 20 mM phosphoric acid. Acid traps were removed after the first 6 hours and then after 1, 2, 3, 6, 10, and 14 days.

4.2 Appendix B – Data Summary from Study 1

Cow	Diet	Manure	Collection Date	Flux @ 15°C (mg m^{-2} min^{-1})	Mass Lost After 18 hr (mg N)	Total Mass Lost (mg N)	Initial Flux Peak (mg m^{-2} min^{-1})
4017	A	Scrape	9/18/2006	-	366	377	2.00
		Flush	9/21/2006	0.691	78.4	106	0.511
		Sep. Solids	9/21/2006	2.38	285	618	2.14
		Sep. Liquid	9/21/2006	1.61	327	598	1.14
	C	Scrape	8/8/2006	-3.21	1062	1287	5.91
		Flush	8/8/2006	-	569	545	-
		Sep. Solids	8/8/2006	-0.350	408	526	2.38
		Sep. Liquid	8/10/2006	1.42	533	518	2.95
	D	Scrape	8/31/2006	2.78	334	771	2.06
		Flush	8/31/2006	1.17	101	477	1.42
		Sep. Solids	8/31/2006	1.30	532	919	2.89
		Sep. Liquid	8/31/2006	1.94	287	610	0.958
4019	A	Scrape	8/8/2006	1.67	264	1028	2.38
		Flush	8/8/2006	-	230	582	-
		Sep. Solids	8/8/2006	0.284	-	409	2.56
		Sep. Liquid	8/10/2006	2.04	771	794	4.23
	B	Scrape	8/31/2006	3.82	477	1680	3.81
		Flush	8/31/2006	1.22	134	389	0.960
		Sep. Solids	8/31/2006	3.71	407	1051	2.15
		Sep. Liquid	8/31/2006	2.71	385	467	1.95
4093	A	Scrape	8/29/2006	7.75	449	6811	7.26
		Flush	8/29/2006	2.01	150	814	2.04
		Sep. Solids	8/29/2006	3.46	483	513	2.81
		Sep. Liquid	8/31/2006	3.52	556	1415	2.97

Cow	Diet	Manure	Collection Date	Flux @ 15°C (mg m^{-2} min^{-1})	Mass Lost After 18 hr (mg N)	Total Mass Lost (mg N)	Initial Flux Peak (mg m^{-2} min^{-1})
4093	B	Scrape	9/21/2006	1.19	92.6	380	1.21
		Flush	9/18/2006	1.02	23.1	139	0.309
		Sep. Solids	9/18/2006	1.18	122	402	0.636
		Sep. Liquid	9/21/2006	1.16	129	624	0.633
	D	Scrape	8/8/2006	-	451	773	-
		Flush	8/8/2006	1.30	159	1758	1.74
		Sep. Solids	8/10/2006	0.871	570	711	3.61
		Sep. Liquid	8/10/2006	2.49	522	1245	2.77

Cow	Diet	Manure	Flux Curve Slope @ t_0 [(mg m^{-2} min^{-1}) min^{-1}]	Ave. T for 1st 18 hr (^oC)	Test Length (hr)	M_{urine} (kg)	M_{feces} (kg)
4017	A	Scrape	5.02E-03	8.81	18.4	3.02	11.2
		Flush	4.97E-03	9.35	24.2	4.42	10.8
		Sep. Solids	1.44E-02	8.52	41.6	8.98	21.7
		Sep. Liquid	1.07E-02	13.7	40.1	8.98	21.7
	C	Scrape	1.63E-02	25.0	22.0	4.85	12.0
		Flush	3.30E-03	24.4	17.5	4.81	12.0
		Sep. Solids	2.15E-02	22.8	26.3	9.84	24.0
		Sep. Liquid	5.18E-02	18.0	17.4	7.44	14.4
	D	Scrape	5.32E-03	9.30	38.2	3.86	9.07
		Flush	3.15E-04	13.9	45.1	3.86	9.12
		Sep. Solids	1.11E-02	16.7	43.0	7.39	17.7
		Sep. Liquid	7.07E-03	10.3	37.9	7.39	17.7
4019	A	Scrape	1.84E-03	18.3	44.7	7.89	13.2
		Flush	7.32E-04	21.2	28.8	7.53	11.6
		Sep. Solids	1.78E-02	19.3	13.5	15.5	26.6
		Sep. Liquid	4.67E-02	19.0	18.7	12.1	19.5
	B	Scrape	4.52E-03	11.7	47.7	4.40	8.57
		Flush	1.21E-03	13.5	43.1	4.40	8.57
		Sep. Solids	1.39E-02	2.65	46.6	8.57	16.9
		Sep. Liquid	4.41E-03	5.31	21.7	8.57	16.9
4093	A	Scrape	2.52E-03	7.98	97.4	5.58	8.03
		Flush	8.14E-04	13.1	46.7	5.44	8.07
		Sep. Solids	1.77E-02	9.79	19.5	11.9	16.2
		Sep. Liquid	7.58E-03	9.75	52.4	8.75	15.2
	B	Scrape	3.00E-04	5.95	40.1	3.49	8.89
		Flush	1.84E-04	8.47	72.1	8.85	10.0
		Sep. Solids	3.75E-03	-0.100	73.3	6.99	17.9
		Sep. Liquid	2.07E-03	2.08	73.6	6.99	17.9

Cow	Diet	Manure	Flux Curve Slope @ t_0 [(mg m^{-2} min^{-1}) min^{-1}]	Ave. T for 1st 18 hr (^oC)	Test Length (hr)	M_{urine} (kg)	M_{feces} (kg)
4093	D	Scrape	3.71E-03	16.6	24.4	3.95	8.48
		Flush	6.78E-04	22.5	98.1	3.95	8.48
		Sep. Solids	3.77E-02	19.2	27.0	6.17	10.8
		Sep. Liquid	2.30E-02	13.8	44.0	6.12	10.8

Cow	Diet	Manure	M_{water} (kg)	M_{sample} (Before) (kg)	M_{sample} (After) (kg)	TKN_0[a] (mg N L^{-1})	TKN_f (mg N L^{-1})
4017	A	Scrape	-	14.1	14.0	4476	4446
		Flush	61.0	22.0	21.9	1012	852
		Sep. Solids	122	6.76	6.62	2.00	1.86
		Sep. Liquid	122	20.5	20.3	1127	1074
	C	Scrape	-	16.6	16.1	4332	3638
		Flush	67.2	21.5	21.5	1388	1152
		Sep. Solids	134	4.85	4.72	1.68	1.25
		Sep. Liquid	87.0	22.0	21.6	975	800
	D	Scrape	-	12.7	12.6	3925	3818
		Flush	51.4	20.6	20.5	861	916
		Sep. Solids	103	2.81	2.72	1.85	1.64
		Sep. Liquid	103	21.4	21.2	1074	1004
4019	A	Scrape	-	21.0	20.8	4090	3915
		Flush	76.5	22.5	22.2	1463	1182
		Sep. Solids	168	4.81	4.76	1.20	1.12
		Sep. Liquid	125	21.4	21.2	1132	1129
	B	Scrape	-	12.8	12.6	4439	3875
		Flush	51.6	20.3	20.0	1190	1148
		Sep. Solids	103	3.72	3.58	2.38	2.11
		Sep. Liquid	103	18.6	18.6	1482	1514
4093	A	Scrape	-	13.4	13.2	5556	5073
		Flush	54.2	19.5	19.3	1425	1391
		Sep. Solids	105	8.21	8.16	2.29	2.09
		Sep. Liquid	105	21.5	21.5	1357	1150
	B	Scrape	-	12.2	12.0	7603	6846
		Flush	78.8	21.2	20.8	1320	1308
		Sep. Solids	99.0	6.89	6.71	2.10	1.92
		Sep. Liquid	99.0	21.0	20.8	1074	1013

Cow	Diet	Manure	M_{water} (kg)	M_{sample} (Before) (kg)	M_{sample} (After) (kg)	TKN_0[a] (mg N L^{-1})	TKN_f (mg N L^{-1})
4093	D	Scrape	-	12.3	12.3	3998	3924
		Flush	49.7	19.3	18.9	1070	769
		Sep. Solids	67.8	2.13	2.00	1.68	1.22
		Sep. Liquid	67.9	21.3	21.0	1280	1124

[a]TKN values for separated solids manure are in units of mg N (g solids)$^{-1}$

Cow	Diet	Manure	% Recovery (%)	pH_0	pH_f	U/F Ratio	U/Sample Ratio	M_{feces} (kg)
4017	A	Scrape	45.7%	6.4	8.0	0.27	0.211	11.1
		Flush	2.95%	7.0	8.6	0.41	0.058	3.12
		Sep. Solids	51.5%	8.8	-	0.41	-	21.7
		Sep. Liquid	46.8%	8.5	8.4	0.41	-	21.7
	C	Scrape	9.51%	7.1	7.5	0.41	0.288	11.8
		Flush	10.5%	7.1	8.5	0.40	0.057	3.08
		Sep. Solids	23.3%	8.6	8.7	0.41	-	24.0
		Sep. Liquid	12.6%	8.5	8.6	0.52	-	14.4
	D	Scrape	40.9%	6.5	7.8	0.43	0.298	8.9
		Flush	-45.3%	6.6	8.5	0.42	0.060	2.92
		Sep. Solids	124%	8.9	9.1	0.42	-	17.7
		Sep. Liquid	36.3%	8.4	8.4	0.42	-	17.7
4019	A	Scrape	24.0%	6.5	7.2	0.60	0.374	13.1
		Flush	8.69%	6.9	8.7	0.65	0.079	2.73
		Sep. Solids	93.9%	8.4	9.1	0.58	-	26.6
		Sep. Liquid	365%	8.7	8.7	0.62	-	19.5
	B	Scrape	21.5%	6.9	7.8	0.51	0.339	8.5
		Flush	35.0%	7.0	8.9	0.51	0.068	2.69
		Sep. Solids	81.4%	9.3	9.3	0.51	-	16.9
		Sep. Liquid	-88.5%	8.8	8.7	0.51	-	16.9
4093	A	Scrape	92.0%	7.2	8.8	0.69	0.410	7.9
		Flush	88.9%	-	8.9	0.67	0.080	2.33
		Sep. Solids	29.5%	9.1	9.1	0.74	-	16.2
		Sep. Liquid	31.0%	8.8	8.8	0.58	-	15.2
	B	Scrape	3.81%	6.7	8.3	0.39	0.282	8.7
		Flush	17.6%	7.3	8.6	0.89	0.091	2.17
		Sep. Solids	25.3%	8.6	8.5	0.39	-	17.9
		Sep. Liquid	44.1%	8.7	8.5	0.39	-	17.9

Cow	Diet	Manure	% Recovery (%)	pH_0	pH_f	U/F Ratio	U/Sample Ratio	M_{feces} (kg)
4093	D	Scrape	81.9%	7.3	8.4	0.47	0.318	8.4
		Flush	28.8%	6.9	8.2	0.47	0.064	2.63
		Sep. Solids	62.0%	9.1	8.8	0.57	-	10.8
		Sep. Liquid	34.8%	8.5	8.5	0.57	-	10.8

Cow	Diet	Manure	TKN_{feces} (mg N g^{-1})	$M_{feces\text{-}N}$ (g N)	M_{urine} (kg)	TKN_{urine} (mg N L^{-1})	$M_{urine\text{-}N}$ (g N)
4017	A	Scrape	-	-	2.97	-	-
		Flush	28.7	89.5	1.28	15014	19.2
		Sep. Solids	29.2	634	8.98	15014	135
		Sep. Liquid	29.2	634	8.98	15014	135
	C	Scrape	24.0	285	4.80	10124	48.6
		Flush	24.0	74.1	1.23	10124	12.5
		Sep. Solids	24.0	578	9.84	10124	99.6
		Sep. Liquid	28.0	402	7.44	20848	155
	D	Scrape	27.1	242	3.80	13527	51.4
		Flush	27.1	79.1	1.24	13527	16.7
		Sep. Solids	27.1	480	7.39	13527	100
		Sep. Liquid	27.1	480	7.39	13527	100
4019	A	Scrape	28.1	369	7.84	8808	69
		Flush	28.1	76.8	1.77	8808	15.6
		Sep. Solids	28.1	748	15.5	8808	136
		Sep. Liquid	27.6	537	12.1	-	-
	B	Scrape	28.5	241	4.34	28398	123
		Flush	28.5	76.8	1.38	28398	39.2
		Sep. Solids	28.5	481	8.57	28398	243
		Sep. Liquid	28.5	481	8.57	28398	243
4093	A	Scrape	24.8	196	5.50	16701	92
		Flush	24.8	57.6	1.57	16701	26.2
		Sep. Solids	24.8	401	11.9	16701	199
		Sep. Liquid	26.2	398	8.75	28598	250
	B	Scrape	26.3	229.5	3.43	22163	76
		Flush	-	-	1.92	-	-
		Sep. Solids	-	-	6.99	-	-
		Sep. Liquid	26.3	470	6.99	22163	155

Cow	Diet	Manure	TKN_{feces} (mg N g^{-1})	$M_{feces\text{-}N}$ (g N)	M_{urine} (kg)	TKN_{urine} (mg N L^{-1})	$M_{urine\text{-}N}$ (g N)
4093	D	Scrape	24.7	207.3	3.90	27740	108
		Flush	24.7	65.1	1.22	27740	34.0
		Sep. Solids	28.3	305	6.17	-	-
		Sep. Liquid	28.3	305	6.12	-	-

4.3 Appendix C – Data Summary from Study 2

Cow	Diet	Manure	Collection Date	Mass Lost After 18 hr (mg N)	Total Mass Lost (mg N)	Ave. T for 1st 18 hr (^{o}C)	Test Length (hr)
3978	A	Scrape	3/20/2007	1687	2582	19.0	24.7
		Flush	3/20/2007	290	509	17.1	24.8
		Sep. Solids	3/20/2007	267	300	18.3	20.5
		Sep. Liquid	3/20/2007	241	278	17.1	20.5
	C	Scrape	2/10/2007	450	2692	14.6	46.2
		Flush	2/10/2007	207	243	18.8	19.9
		Sep. Solids	2/10/2007	353	432	14.0	22.7
		Sep. Liquid	2/10/2007	832	1020	23.2	21.5
	D	Scrape	3/1/2007	404	535	12.5	21.7
		Flush	3/1/2007	85.0	120	14.5	21.7
		Sep. Solids	3/1/2007	292	355	10.4	22.9
		Sep. Liquid	3/1/2007	271	363	12.8	22.9
3984	B	Scrape	2/10/2007	432	450	10.1	18.4
		Flush	2/10/2007	267	193	17.4	15.6
		Sep. Solids	2/10/2007	541	780	13.3	27.2
		Sep. Liquid	2/10/2007	705	686	16.4	18.0
	C	Scrape	3/1/2007	598	2686	13.3	42.5
		Flush	3/1/2007	143	595	14.9	42.5
		Sep. Solids	3/1/2007	458	703	15.8	27.0
		Sep. Liquid	3/1/2007	405	624	15.8	27.0
	D	Scrape	3/20/2007	951	854	16.6	16.3
		Flush	3/20/2007	213	162	16.5	16.5
		Sep. Solids	3/20/2007	552	693	17.8	22.2
		Sep. Liquid	3/20/2007	490	601	16.8	22.2

Cow	Diet	Manure	Collection Date	Mass Lost After 18 hr (mg N)	Total Mass Lost (mg N)	Ave. T for 1st 18 hr (^{o}C)	Test Length (hr)
3988	B	Scrape	3/20/2007	1685	3100	16.8	27.9
		Flush	3/20/2007	173	384	15.9	27.9
		Sep. Solids	3/20/2007	398	324	14.8	14.4
		Sep. Liquid	3/20/2007	361	285	14.5	14.4
	C	Scrape	4/5/2007	2343	2671	17.9	19.6
		Flush	4/5/2007	318	375	17.3	19.6
		Sep. Solids	4/5/2007	713	850	19.4	22.2
		Sep. Liquid	4/5/2007	577	704	18.2	22.2
	D	Scrape	2/10/2007	1014	1032	17.9	18.2
		Flush	2/10/2007	104	128	15.8	19.9
		Sep. Solids	2/10/2007	137	155	11.2	21.2
		Sep. Liquid	2/10/2007	254	342	17.2	22.2
4016	A	Scrape	2/10/2007	871	990	16.5	19.3
		Flush	2/10/2007	263	301	19.3	19.3
		Sep. Solids	2/10/2007	705	680	18.1	18.0
		Sep. Liquid	2/10/2007	670	648	18.5	18.0
	B	Scrape	3/1/2007	825	1028	16.2	19.3
		Flush	3/1/2007	184	223	16.7	20.2
		Sep. Solids	3/1/2007	261	342	15.7	23.6
		Sep. Liquid	3/1/2007	237	318	16.1	23.6
	D	Scrape	4/5/2007	1482	2098	19.2	22.6
		Flush	4/5/2007	256	394	18.8	22.6
		Sep. Solids	4/5/2007	482	573	20.2	22.0
		Sep. Liquid	4/5/2007	422	520	19.5	22.0

Cow	Diet	Manure	M_{urine} (kg)	M_{feces} (kg)	M_{water} (kg)	M_{sample} (Before) (kg)	M_{sample} (After) (kg)
3978	A	Scrape	2.72	5.44	-	7.94	7.71
		Flush	2.74	5.47	32.7	16.1	15.9
		Sep. Solids	5.53	10.9	65.3	3.76	3.67
		Sep. Liquid	5.53	10.9	65.3	17.7	17.6
	C	Scrape	2.72	5.44	-	7.98	7.42
		Flush	2.74	5.44	32.7	19.6	19.3
		Sep. Solids	5.47	10.9	65.3	4.51	4.13
		Sep. Liquid	5.60	10.9	65.4	17.9	17.4
	D	Scrape	2.74	5.44	-	7.92	7.48
		Flush	2.83	5.44	32.7	17.7	17.7
		Sep. Solids	5.47	10.9	65.3	3.33	3.15
		Sep. Liquid	5.47	10.9	65.3	16.0	15.6
3984	B	Scrape	2.72	5.44	-	7.94	7.67
		Flush	2.72	5.44	32.7	18.6	18.1
		Sep. Solids	5.47	10.9	65.3	3.58	3.42
		Sep. Liquid	5.44	11.0	65.3	21.4	21.0
	C	Scrape	2.72	5.44	-	7.96	7.30
		Flush	2.72	5.42	32.7	18.1	17.5
		Sep. Solids	4.54	10.9	65.4	4.31	4.03
		Sep. Liquid	4.54	10.9	65.4	17.6	17.3
	D	Scrape	2.74	5.44	-	7.96	7.69
		Flush	2.74	5.42	32.8	18.1	18.0
		Sep. Solids	5.47	10.9	65.3	4.83	4.65
		Sep. Liquid	5.47	10.9	65.3	18.0	17.8
3988	B	Scrape	2.70	5.47	-	7.94	7.51
		Flush	2.75	5.42	32.7	18.4	18.1
		Sep. Solids	5.42	10.9	65.3	4.06	3.90
		Sep. Liquid	5.42	10.9	65.3	18.2	18.1

Cow	Diet	Manure	M_{urine} (kg)	M_{feces} (kg)	M_{water} (kg)	M_{sample} (Before) (kg)	M_{sample} (After) (kg)
3988	C	Scrape	2.68	5.44	-	7.89	7.78
		Flush	1.63	3.27	19.7	17.6	17.5
		Sep. Solids	5.40	10.9	65.3	4.90	4.81
		Sep. Liquid	5.40	10.9	65.3	18.1	18.0
	D	Scrape	2.72	5.44	-	7.96	7.85
		Flush	2.77	5.44	32.7	19.1	19.1
		Sep. Solids	5.44	10.9	65.3	4.35	4.20
		Sep. Liquid	5.47	10.9	65.3	19.0	18.6
4016	A	Scrape	2.74	5.44	-	7.96	7.96
		Flush	2.70	5.42	32.7	17.3	17.1
		Sep. Solids	5.44	10.9	65.3	4.13	4.13
		Sep. Liquid	5.44	10.9	65.3	17.4	17.3
	B	Scrape	2.70	5.44	-	7.76	7.42
		Flush	2.79	5.44	32.7	16.5	16.3
		Sep. Solids	5.42	10.9	65.3	3.74	3.54
		Sep. Liquid	5.42	10.9	65.3	17.7	17.4
	D	Scrape	2.72	5.47	-	7.92	7.92
		Flush	1.36	2.74	16.4	15.7	15.4
		Sep. Solids	5.44	10.9	65.3	4.20	4.20
		Sep. Liquid	5.44	10.9	65.3	18.1	18.1

Cow	Diet	Manure	TKN_0[a] (mg N L^{-1})	TKN_f (mg N L^{-1})	TAN_0 (mg N L^{-1})	TAN_f (mg N L^{-1})	% Recovery (%)
3978	A	Scrape	6192	3384	3885	2493	11.2%
		Flush	1636	1620	63.5	879	99.0%
		Sep. Solids	2.04	2.49	381	278	-20.4%
		Sep. Liquid	1075	1048	478	510	46.7%
	C	Scrape	5927	4186	2465	3470	16.5%
		Flush	1665	1657	50.5	689	30.5%
		Sep. Solids	2.20	2.18	523	582	46.4%
		Sep. Liquid	1850	1756	844	1317	41.2%
	D	Scrape	6223	5697	2055	2887	8.1%
		Flush	1511	1455	53.5	461	12.1%
		Sep. Solids	2.44	2.92	569	632	-33.2%
		Sep. Liquid	1712	1679	642	867	31.9%
3984	B	Scrape	8918	6869	6170	5960	2.5%
		Flush	1750	1731	76.0	824	14.9%
		Sep. Solids	2.74	2.68	869	912	121.8%
		Sep. Liquid	1811	1672	811	1158	18.7%
	C	Scrape	7377	6309	635	4017	21.2%
		Flush	1511	1455	58.0	707	31.2%
		Sep. Solids	2.39	2.82	714	726	-65.5%
		Sep. Liquid	1552	1525	926	969	70.1%
	D	Scrape	5896	5814	2160	2475	38.2%
		Flush	1293	1272	106	582	29.2%
		Sep. Solids	2.45	2.43	747	689	128.9%
		Sep. Liquid	1598	1521	764	947	37.8%
3988	B	Scrape	6981	5382	4035	4890	20.7%
		Flush	1695	1608	98.0	706	17.9%
		Sep. Solids	2.51	2.70	527	564	-94.5%
		Sep. Liquid	1234	1198	588	732	34.8%

Cow	Diet	Manure	TKN_0[a] (mg N L^{-1})	TKN_f (mg N L^{-1})	TAN_0 (mg N L^{-1})	TAN_f (mg N L^{-1})	% Recovery (%)
3988	C	Scrape	8201	6759	6420	5413	22.0%
		Flush	1724	1806	130	1135	-30.3%
		Sep. Solids	2.50	2.39	-	-	112.5%
		Sep. Liquid	1392	1295	731	956	38.2%
	D	Scrape	4248	4013	6150	5390	44.4%
		Flush	1732	1748	81.0	671	-48.1%
		Sep. Solids	2.22	2.21	393	349	39.3%
		Sep. Liquid	1479	1474	383	697	49.1%
4016	A	Scrape	6169	5335	3507	3687	14.9%
		Flush	1400	1389	84.0	645	68.0%
		Sep. Solids	2.52	2.35	771	762	96.9%
		Sep. Liquid	1678	1689	839	1299	-850.6%
	B	Scrape	7318	6730	2230	3450	15.0%
		Flush	1934	1922	69.0	559	44.3%
		Sep. Solids	2.32	2.47	467	318	-598.4%
		Sep. Liquid	1164	1131	294	506	34.7%
	D	Scrape	5602	4402	4050	4280	22.1%
		Flush	1377	1378	80.0	747	100.9%
		Sep. Solids	2.06	2.26	633	497	-68.3%
		Sep. Liquid	1235	1185	627	543	55.7%

[a]TKN values for separated solids manure are in units of mg N (g solids)$^{-1}$

Cow	Diet	Manure	pH_0	pH_f	U/F Ratio	U/Sample Ratio	M_{feces} (kg)
3978	A	Scrape	6.9	8.5	0.50	0.33	5.29
		Flush	7.0	8.7	0.50	0.07	2.15
		Sep. Solids	8.3	8.8	0.51	-	10.9
		Sep. Liquid	8.2	7.9	0.51	-	10.9
	C	Scrape	6.8	8.7	0.50	0.33	5.32
		Flush	7.1	8.5	0.50	0.07	2.61
		Sep. Solids	8.7	9.1	0.50	-	10.9
		Sep. Liquid	8.7	8.7	0.51	-	10.9
	D	Scrape	6.8	8.4	0.50	0.34	5.26
		Flush	6.9	8.4	0.52	0.07	2.35
		Sep. Solids	8.5	8.8	0.50	-	10.9
		Sep. Liquid	8.5	8.4	0.50	-	10.9
3984	B	Scrape	7.1	8.6	0.50	0.33	5.29
		Flush	7.2	8.5	0.50	0.07	2.49
		Sep. Solids	7.6	9.0	0.50	-	10.9
		Sep. Liquid	8.8	8.7	0.50	-	11.0
	C	Scrape	6.2	8.6	0.50	0.33	5.31
		Flush	6.5	8.4	0.50	0.07	2.40
		Sep. Solids	8.5	8.9	0.42	-	10.9
		Sep. Liquid	8.4	8.2	0.42	-	10.9
	D	Scrape	6.4	8.5	0.50	0.34	5.29
		Flush	7.1	8.6	0.51	0.07	2.40
		Sep. Solids	8.9	8.9	0.50	-	10.9
		Sep. Liquid	8.6	8.4	0.50	-	10.9
3988	B	Scrape	6.9	8.8	0.49	0.33	5.31
		Flush	7.3	8.7	0.51	0.07	2.45
		Sep. Solids	8.7	8.8	0.50	-	10.9
		Sep. Liquid	8.5	8.6	0.50	-	10.9

Cow	Diet	Manure	pH_0	pH_f	U/F Ratio	U/Sample Ratio	M_{feces} (kg)
3988	C	Scrape	7.1	8.9	0.49	0.33	5.29
		Flush	7.5	8.7	0.50	0.07	2.34
		Sep. Solids	8.3	8.8	0.50	-	10.9
		Sep. Liquid	8.7	8.5	0.50	-	10.9
	D	Scrape	7.5	8.6	0.50	0.33	5.31
		Flush	7.4	8.7	0.51	0.07	2.55
		Sep. Solids	8.6	8.6	0.50	-	10.9
		Sep. Liquid	8.6	8.4	0.50	-	10.9
4016	A	Scrape	7.2	8.6	0.50	0.34	5.29
		Flush	7.5	8.6	0.50	0.07	2.30
		Sep. Solids	8.4	9.0	0.50	-	10.9
		Sep. Liquid	-	8.6	0.50	-	10.9
	B	Scrape	6.7	8.5	0.50	0.33	5.19
		Flush	7.0	8.5	0.51	0.07	2.19
		Sep. Solids	8.5	8.8	0.50	-	10.9
		Sep. Liquid	8.2	8.0	0.50	-	10.9
	D	Scrape	7.3	8.4	0.50	0.33	5.28
		Flush	6.9	8.2	0.50	0.07	2.11
		Sep. Solids	9.1	8.8	0.50	-	10.9
		Sep. Liquid	8.5	8.5	0.50	-	10.9

Cow	Diet	Manure	TKN_{feces} (mg N g^{-1})	$M_{feces\text{-}N}$ (g N)	M_{urine} (kg)	TKN_{urine} (mg N L^{-1})	$M_{urine\text{-}N}$ (g N)
3978	A	Scrape	29.9	-	2.65	21870	57.9
		Flush	29.9	64.3	1.08	21870	23.6
		Sep. Solids	29.9	326	5.53	21870	121
		Sep. Liquid	29.9	326	5.53	21870	121
	C	Scrape	28.1	149	2.66	32528	86.6
		Flush	28.1	73.3	1.32	32528	42.8
		Sep. Solids	28.1	305	5.47	32528	178
		Sep. Liquid	28.1	307	5.60	32528	182
	D	Scrape	28.7	151	2.65	32182	85.4
		Flush	28.7	67.3	1.22	32182	39.3
		Sep. Solids	28.7	312	5.47	32182	176
		Sep. Liquid	28.7	312	5.47	32182	176
3984	B	Scrape	26.7	141	2.65	35397	93.7
		Flush	26.7	66.2	1.24	35397	44.0
		Sep. Solids	26.7	290	5.47	35397	193
		Sep. Liquid	26.7	292	5.44	35397	193
	C	Scrape	26.7	141	2.65	27482	72.9
		Flush	26.7	64.1	1.21	27482	33.2
		Sep. Solids	26.7	291	4.54	27482	125
		Sep. Liquid	26.7	291	4.54	27482	125
	D	Scrape	25.4	134	2.67	26179	69.9
		Flush	25.4	60.9	1.21	26179	31.8
		Sep. Solids	25.4	277	5.47	26179	143
		Sep. Liquid	25.4	277	5.47	26179	143
3988	B	Scrape	27.6	146.8	2.62	27695	72.7
		Flush	27.6	-	1.24	27695	34.4
		Sep. Solids	27.6	-	5.42	27695	150
		Sep. Liquid	27.6	300	5.42	27695	150

Cow	Diet	Manure	TKN_{feces} (mg N g^{-1})	$M_{feces\text{-}N}$ (g N)	M_{urine} (kg)	TKN_{urine} (mg N L^{-1})	$M_{urine\text{-}N}$ (g N)
3988	C	Scrape	24.7	130.8	2.60	29571	76.9
		Flush	24.7	57.7	1.17	29571	34.5
		Sep. Solids	24.7	269	5.40	29571	160
		Sep. Liquid	24.7	269	5.40	29571	160
	D	Scrape	27.4	145	2.65	30842	81.8
		Flush	27.4	69.8	1.29	30842	39.9
		Sep. Solids	27.4	299	5.44	30842	168
		Sep. Liquid	27.4	298	5.47	30842	169
4016	A	Scrape	28.1	149	2.67	17277	46.1
		Flush	28.1	64.4	1.14	17277	19.8
		Sep. Solids	28.1	305	5.44	17277	94
		Sep. Liquid	28.1	305	5.44	17277	94
	B	Scrape	28.6	148.4	2.57	26531	68.2
		Flush	28.6	-	1.12	26531	29.8
		Sep. Solids	28.6	-	5.42	26531	144
		Sep. Liquid	28.6	312	5.42	26531	144
	D	Scrape	25.1	132.5	2.63	19798	52.1
		Flush	25.1	52.9	1.05	19798	20.7
		Sep. Solids	25.1	273	5.44	19798	108
		Sep. Liquid	25.1	273	5.44	19798	108

4.4 Appendix D – Data used in determining handling effects

Cow	Diet	Manure	Mass Lost after 18 hr (mg N)	Ave. Temp for 1st 18 hr (K)	Mass Lost Corr. to 15°C (mg N)
3978	A	Scrape	1687	292	1384
		Flush	290	290	261
	C	Scrape	450	288	458
		Flush	207	292	171
	D	Scrape	404	286	457
		Flush	85	288	86.9
3984	B	Scrape	432	283	553
		Flush	267	290	237
	C	Scrape	598	286	649
		Flush	143	288	143
	D	Scrape	951	290	877
		Flush	213	290	197
3988	B	Scrape	1685	290	1539
		Flush	173	289	165
	C	Scrape	2343	291	2028
		Flush	318	290	283
	D	Scrape	1014	291	878
		Flush	104	289	100
4016	A	Scrape	871	290	807
		Flush	263	292	213
	B	Scrape	825	289	776
		Flush	184	290	169
	D	Scrape	1482	292	1204
		Flush	256	292	212

Cow	Diet	Manure	Mass Lost after 18 hr (mg N)	Ave. Temp for 1st 18 hr (K)	Mass Lost Corr. to 15°C (mg N)
4017	A	Scrape	366	282	500
		Flush	78.4	282	104
	C	Scrape	1062	298	656
		Flush	569	297	362
	D	Scrape	334	282	445
		Flush	101	287	106
4019	A	Scrape	264	291	224
		Flush	230	294	170
	B	Scrape	477	285	562
		Flush	134	287	144
4093	A	Scrape	449	281	640
		Flush	150	286	165
	B	Scrape	92.6	279	147
		Flush	23.1	281	32.1
	D	Scrape	451	290	416
		Flush	159	296	110

Cow	Diet	Manure	Mass Lost after 18 hr (mg N)	Ave. Temp for 1st 18 hr (K)	Mass Lost Corr. to 15°C (mg N)
3978	A	Sep. Solids	267	291	227
		Sep. Liquid	241	290	217
	C	Sep. Solids	353	287	370
		Sep. Liquid	832	296	559
	D	Sep. Solids	292	283	367
		Sep. Liquid	271	286	302
3984	B	Sep. Solids	541	286	588
		Sep. Liquid	705	289	656
	C	Sep. Solids	458	289	439
		Sep. Liquid	405	289	388
	D	Sep. Solids	552	291	480
		Sep. Liquid	490	290	447
3988	B	Sep. Solids	398	288	401
		Sep. Liquid	361	288	369
	C	Sep. Solids	713	292	574
		Sep. Liquid	577	291	492
	D	Sep. Solids	137	284	165
		Sep. Liquid	254	290	228
4016	A	Sep. Solids	705	291	604
		Sep. Liquid	670	292	563
	B	Sep. Solids	261	289	252
		Sep. Liquid	237	289	224
	D	Sep. Solids	482	293	373
		Sep. Liquid	422	293	338
4017	A	Sep. Solids	285	282	395
		Sep. Liquid	327	287	348
	C	Sep. Solids	408	296	279
		Sep. Liquid	533	291	459

Cow	Diet	Manure	Mass Lost after 18 hr (mg N)	Ave. Temp for 1st 18 hr (K)	Mass Lost Corr. to 15°C (mg N)
4017	D	Sep. Solids	532	290	488
		Sep. Liquid	287	283	364
4019	B	Sep. Solids	407	276	770
		Sep. Liquid	385	278	632
4093	A	Sep. Solids	483	283	627
		Sep. Liquid	556	283	723
	B	Sep. Solids	122	273	268
		Sep. Liquid	129	275	252
	D	Sep. Solids	570	292	463
		Sep. Liquid	522	287	553

4.5 Appendix E – Data used in determining $\frac{\text{Mass}_{9\text{-}18hr}}{\text{Mass}_{0\text{-}9hr}}$ values

Red represents outliers excluded from analysis

Scrapes

Cow	Diet	Mass After 1st 9 hr (mg N)	After 18 hr (mg N)	After 2nd 9 hr (mg N)	Ave. T for 1st 9 hr (K)	for 2nd 9 hr (K)	Mass Corr. 1st 9 hr (mg N)	After 2nd 9 hr (mg N)
3978	A	566	1687	1121	292	292	464	920
	C	110	450	340	287	287	115	351
	D	131	404	273	284	287	157	292
3984	B	132	432	300	283	283	168	388
	C	139	598	459	286	287	156	479
	D	390	951	561	289	290	369	502
3988	B	580	1685	1105	291	289	504	1060
	C	723	2343	1620	291	291	626	1395
	D	264	1014	750	291	291	228	652
4016	A	241	871	630	290	289	221	587
	B	224	825	601	289	290	214	554
	D	432	1482	1050	292	292	354	845
4017	A	139	366	227	283	281	179	328
	C	526	1062	536	299	297	310	347
	D	130	334	204	282	282	172	274
4019	A	81.0	264	183	291	292	69.1	154
	B	182	477	295	286	283	200	375
4093	A	158	449	291	282	280	214	438
	B	36.4	92.6	56.2	281	277	52.1	98.7
	D	109	451	342	289	290	101	314

Flushes

Cow	Diet	Mass After 1st 9 hr (mg N)	After 18 hr (mg N)	After 2nd 9 hr (mg N)	Ave. T for 1st 9 hr (K)	for 2nd 9 hr (K)	Mass Corr. 1st 9 hr (mg N)	After 2nd 9 hr (mg N)
3978	A	89.0	290	201	290	291	81.3	177
	C	59.0	207	148	293	291	46.8	125
	D	28.2	85.0	56.8	289	286	27.3	61.4
3984	B	62.0	267	205	290	291	56.6	174
	C	42.0	143	101	288	288	42.5	100
	D	94.0	213	119	289	290	88.4	108
3988	B	56.0	173	117	289	289	52.9	113
	C	85.0	318	233	290	290	76.1	208
	D	32.0	104	72.0	289	289	30.7	68.7
4016	A	70.0	263	193	292	292	56.6	155
	B	55.0	184	129	290	290	51.0	117
	D	67.0	256	189	292	292	56.3	154
4017	A	40.2	78.4	38.2	285	280	**47.8**	**56.7**
	C	204	569	365	299	296	122	246
	D	41.0	101	60.0	287	287	43.0	63.6
4019	A	70.8	230	159.2	297	291	45.4	136
	B	44.0	134	90.0	288	285	43.3	106
4093	A	48.0	150	102	287	285	50.1	117
	D	58.0	159	101	298	293	36.3	77.9

Sep. Solids

Cow	Diet	Mass After 1st 9 hr (mg N)	After 18 hr (mg N)	After 2nd 9 hr (mg N)	Ave. T for 1st 9 hr (K)	for 2nd 9 hr (K)	Mass Corr. 1st 9 hr (mg N)	After 2nd 9 hr (mg N)
3978	A	107	267	160	291	291	91.3	135
	C	197	353	156	288	287	196	168
	D	158	292	134	284	283	196	170
3984	B	294	541	247	287	286	304	270
	C	242	458	216	288	289	238	202
	D	288	552	264	290	291	255	224
3988	B	214	398	184	288	288	218	184
	C	374	713	339	292	293	313	264
	D	74.0	137	63	284	284	88.5	75.7
4016	A	378	705	327	291	291	322	283
	B	137	261	124	289	288	129	121
	D	249	482	233	293	294	196	178
4017	A	140	285	145	284	279	**170**	**230**
	C	239	408	169	297	295	154	122
	D	302	532	230	290	289	273	214
4019	B	228	407	179	277	274	399	367
4093	A	277	483	206	284	281	336	287
	D	357	570	213	294	291	271	186

Sep. Liquid

Cow	Diet	Mass After 1st 9 hr (mg N)	After 18 hr (mg N)	After 2nd 9 hr (mg N)	Ave. T for 1st 9 hr (K)	for 2nd 9 hr (K)	Mass Corr. 1st 9 hr (mg N)	After 2nd 9 hr (mg N)
3978	A	116	241	125	290	290	104	112
	C	386	832	446	297	296	255	303
	D	125	271	146	286	286	141	161
3984	B	264	705	441	288	291	260	387
	C	195	405	210	288	289	192	197
	D	247	490	243	290	290	228	220
3988	B	163	361	198	287	288	169	200
	C	291	577	286	291	292	252	239
	D	82	254	172	288	291	81.4	145
4016	A	312	670	358	292	291	261	302
	B	115	237	122	289	289	108	116
	D	180	422	242	293	293	144	194
4017	A	136	327	191	285	288	157	187
	C	296	533	237	292	290	245	212
	D	127	287	160	283	284	166	196
4019	A	423	771	348	293	291	332	300
	B	205	385	180	279	277	317	313
4093	A	322	556	234	285	281	379	336
	B	65	129	64.0	276	274	120	132
	D	294	522	228	289	285	286	264

4.6 Appendix F – Data used in Figure 3.5, Figure 3.6, Figure 3.7, and Figure 3.8

Red represents the exclusion of data when the |standardized residual| > |2|

Scrapes

Mass Lost after 18 hr (mg N)	Ave. Temp for 1st 18 hr (K)	Mass Lost Corr. to 15°C (mg N)	Intake (g CP d^{-1})
1687	292	1384	3484
450	288	458	3197
404	286	457	2237
432	283	553	3065
598	286	649	1308
951	290	877	2304
1685	290	1539	2631
2343	291	2028	2649
1014	291	878	1372
871	290	807	3666
825	289	776	2330
1482	292	1204	2618
366	282	500	4090
1062	298	656	2913
334	282	445	3391
264	291	224	3106
477	285	562	1305
449	281	640	3013
92.6	279	147	4173
451	290	416	1395

Flushes

Mass Lost after 18 hr (mg N)	Ave. Temp for 1st 18 hr (K)	Mass Lost Corr. to 15°C (mg N)	Intake (g CP d^{-1})
290	290	261	3484
207	292	171	3197
85.0	288	86.9	2237
267	290	237	3065
143	288	143	1308
213	290	197	2304
173	289	165	2631
318	290	283	2649
104	289	100	1372
263	292	213	3666
184	290	169	2330
256	292	212	2618
78.4	282	104	3996
569	297	**362**	**2913**
101	287	106	3391
230	294	170	3106
134	287	144	1305
150	286	165	3013
23.1	281	**32.1**	**2503**
159	296	110	1395

Sep. Solids

Mass Lost after 18 hr (mg N)	Ave. Temp for 1st 18 hr (K)	Mass Lost Corr. to 15°C (mg N)	Intake (g CP d^{-1})
267	291	227	3484
353	287	370	3197
292	283	367	2237
541	286	588	3065
458	289	439	1308
552	291	480	2304
398	288	401	2631
713	292	574	2649
137	284	165	1372
705	291	604	3666
261	289	252	2330
482	293	373	2618
285	282	395	3996
408	296	279	2913
532	290	488	3391
407	276	**770**	**1305**
483	283	627	3013
122	273	268	2503
570	292	463	2481

Sep. Liquid

Mass Lost after 18 hr (mg N)	Ave. Temp for 1st 18 hr (K)	Mass Lost Corr. to 15°C (mg N)	Intake (g CP d^{-1})
241	290	217	3484
832	296	559	3197
271	286	302	2237
705	289	656	3065
405	289	388	1308
490	290	447	2304
361	288	369	2631
577	291	492	2649
254	290	228	1372
670	292	563	3666
237	289	224	2330
422	293	338	2618
327	287	348	3996
533	291	459	3115
287	283	364	3391
771	292	633	3452
385	278	632	1305
556	283	723	3847
129	275	252	4173

4.7 Appendix G – Data used in Figure 3.9

Cow	Diet	Date	% CP	% DM	Intake (kg)	Intake (g CP d^{-1})	TKN_{urine} (mg N/L)	M_{urine} (kg)	$M_{urine\text{-}N}$ (g N)	TKN_{feces} (mg N/g)	M_{feces} (kg)	$M_{feces\text{-}N}$ (g N)	$M_{T\text{-}N}$ (g N)
3978	A	3/20/07	18	44.1	43.9	3484	21870	19.1	418	29.9	36.2	1084	1502
	C	2/12/07	15.5	44.5	48.1	3319	29726	12.8	382	29.1	45.2	1314	1696
	D	3/1/07	14.5	44.3	35.7	2292	32182	12.1	388	28.7	42.8	1229	1617
	D	3/2/07	14.5	44.3	34.0	2181	25549	13.2	337	28.3	38.5	1088	1425
3984	B	2/12/07	17	44.6	40.2	3048	38468	10.6	407	27.7	31.8	883	1290
	C	3/1/07	15.5	43.8	38.5	2613	27482	10.2	279	26.7	26.3	701	981
	D	3/20/07	14.5	46.3	34.3	2304	26179	14.5	379	25.4	28.0	711	1090
3988	B	3/20/07	17	45.7	29.2	2273	27695	14.0	388	27.6	37.6	1038	1426
	B	3/21/07	17	45.7	38.5	2989	22738	11.5	261	27.3	33.6	917	1178
	C	4/5/07	15.5	45.1	37.9	2649	29571	9.89	292	24.7	47.8	1182	1474
	D	2/12/07	14.5	45.0	4.8	311	21947	9.03	198	27.6	24.4	674	872
4016	A	2/12/07	18	47.3	42.6	3628	26437	16.9	447	27.9	34.2	956	1403
	B	3/2/07	17	44.7	18.3	1392	26531	16.7	443	28.6	36.0	1030	1473
	D	4/5/07	14.5	48.8	37.0	2618	19798	9.80	194	25.1	37.4	937	1131
4017	A	9/21/06	18	54.43	40.8	3996	15014	17.8	267	29.2	43.2	1263	1530
	C	8/8/06	15.5	54.58	34.4	2913	10124	19.5	197	24.0	48.2	1159	1357
	C	8/10/06	15.5	54.58	36.8	3115	20848	14.7	306	28.0	28.8	807	1113
	D	8/31/06	14.5	51.93	45.0	3391	13527	15.1	204	27.1	36.3	983	1187
4019	A	8/8/06	18	51.33	33.6	3106	8808	31.1	274	28.1	53.0	1491	1764
	B	8/31/06	17	49.57	15.5	1305	28398	17.3	492	28.5	34.2	976	1468
4093	A	8/29/06	18	53.71	31.2	3013	16701	21.9	365	24.8	32.3	800	1165
	A	8/31/06	18	53.71	39.8	3847	28598	20.9	597	26.2	31.7	831	1428
	B	9/21/06	17	53.96	45.5	4173	22163	13.9	308	26.3	35.5	934	1242
	D	8/8/06	14.5	54.08	17.8	1395	27740	15.7	435	24.7	33.9	839	1275

4.8 Appendix H – Data used in multiple variable regressions

Red represents the exclusion of data when the |standardized residual| > |2|

Scrapes

Mass Lost After 18 hr (mg N)	Log (Mass)	Ave. T for 1st 18 hr (K)	TKN_0 (mg N L^{-1})	Log(TKN_0)	TAN_0 (mg N L^{-1})	Log(TAN_0)
366	2.56	282	4476	3.65	-	-
1062	3.03	298	4332	3.64	-	-
334	2.52	282	3925	3.59	-	-
264	2.42	291	4090	3.61	-	-
477	2.68	285	4439	3.65	-	-
449	2.65	281	5556	3.74	-	-
92.6	**1.97**	**279**	7603	**3.88**	-	-
451	2.65	290	3998	3.60	-	-
1687	3.23	292	6192	3.79	3885	3.59
450	2.65	288	5927	3.77	2465	3.39
404	2.61	286	6223	3.79	2055	3.31
432	2.64	283	8918	3.95	6170	3.79
598	2.78	286	7377	3.87	635	2.80
951	2.98	290	5896	3.77	2160	3.33
1685	3.23	290	6981	3.84	4035	3.61
2343	3.37	291	8201	3.91	6420	3.81
1014	3.01	291	4248	3.63	6150	3.79
871	2.94	290	6169	3.79	3507	3.54
825	2.92	289	7318	3.86	2230	3.35
1482	3.17	292	5602	3.75	4050	3.61

Flushes

Mass Lost After 18 hr (mg N)	Log (Mass)	Ave. T for 1st 18 hr (K)	TKN_0 (mg N L^{-1})	Log(TKN_0)	TAN_0 (mg N L^{-1})	Log(TAN_0)
78.4	1.89	282	1012	3.01	-	-
569	2.76	297	1388	3.14	-	-
101	2.00	287	861	2.94	-	-
230	2.36	294	1463	3.17	-	-
134	2.13	287	1190	3.08	-	-
150	2.18	286	1425	3.15	-	-
23.1	**1.36**	**281**	1320	**3.12**	-	-
159	**2.20**	**296**	1070	**3.03**	-	-
290	2.46	290	1636	3.21	63.5	1.80
207	2.32	292	1665	3.22	50.5	1.70
85.0	1.93	288	1511	3.18	53.5	1.73
267	2.43	290	1750	3.24	76.0	1.88
143	2.16	288	1511	3.18	58.0	1.76
213	2.33	290	1293	3.11	106	2.03
173	2.24	289	1695	3.23	98.0	1.99
318	2.50	290	1724	3.24	130	2.11
104	2.02	289	1732	3.24	81.0	1.91
263	2.42	292	1400	3.15	84.0	1.92
184	2.26	290	1934	3.29	69.0	1.84
256	2.41	292	1377	3.14	80.0	1.90

Sep. Solids

Mass Lost After 18 hr (mg N)	Log (Mass)	Ave. T for 1st 18 hr (K)	TKN_0 (mg N L^{-1})	$Log(TKN_0)$	TAN_0 (mg N L^{-1})	$Log(TAN_0)$
285	2.45	282	2.00	0.301	-	-
408	2.61	296	1.68	0.225	-	-
532	2.73	290	1.85	0.267	-	-
407	2.61	276	2.38	0.377	-	-
483	2.68	283	2.29	0.360	-	-
122	2.09	273	2.10	0.322	-	-
570	2.76	292	1.68	0.225	-	-
267	2.43	291	2.04	0.310	381	2.58
353	2.55	287	2.20	0.342	523	2.72
292	2.47	283	2.44	0.387	569	2.76
541	2.73	286	2.74	0.438	869	2.94
458	2.66	289	2.39	0.378	714	2.85
552	2.74	291	2.45	0.389	747	2.87
398	2.60	288	2.51	0.400	527	2.72
713	2.85	292	2.50	0.398	-	-
137	2.14	284	2.22	0.346	393	2.59
705	2.85	291	2.52	0.401	771	2.89
261	2.42	289	2.32	0.365	467	2.67
482	2.68	293	2.06	0.314	633	2.80

Sep. Liquid

Mass Lost After 18 hr (mg N)	Log (Mass)	Ave. T for 1st 18 hr (K)	TKN_0 (mg N L^{-1})	$Log(TKN_0)$	TAN_0 (mg N L^{-1})	$Log(TAN_0)$
327	2.51	287	2.00	0.301	-	-
533	2.73	291	1.68	0.225	-	-
287	2.46	283	1.85	0.267	-	-
771	2.89	292	2.38	0.377	-	-
385	2.59	278	2.29	0.360	-	-
556	2.75	283	2.10	0.322	-	-
129	2.11	275	1.68	0.225	-	-
522	2.72	287	2.04	0.310	-	-
241	2.38	290	2.20	0.342	478	2.68
832	2.92	296	2.44	0.387	844	2.93
271	2.43	286	2.74	0.438	642	2.81
705	2.85	289	2.39	0.378	811	2.91
405	2.61	289	2.45	0.389	926	2.97
490	2.69	290	2.51	0.400	764	2.88
361	2.56	288	2.50	0.398	588	2.77
577	2.76	291	2.22	0.346	731	2.86
254	2.40	290	2.52	0.401	383	2.58
670	2.83	292	2.32	0.365	839	2.92
237	2.37	289	2.06	0.314	294	2.47
422	2.63	293	2.00	0.301	627	2.80

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