Ammonia Emissions from Dairy Manure Storage Tanks Affected by Diets and Manure Removal Practices

Lifeng Li

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Dr. Jactone Arogo Ogejo

Dr. Linsey C. Marr

Dr. Katharine F. Knowlton

Dr. Mark D. Hanigan

Dr. Theo A. Dillaha

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Blacksburg, VA

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ABSTRACT

The objectives of this study were to determine: 1) ammonia emission rates from stored scraped and flushed manure from dairy cows fed either normal or low N diet; and 2) seasonal effects on ammonia emission rates from stored scraped and flushed dairy manure. Four pilot-scale tanks were used for manure storage with different treatments - scraped manure for normal diet (NS), flushed manure for normal diet (NF), scraped manure for low N diet (LS), and flushed manure for low N diet (LF). The first part of the study lasted for 1 month and four treatments were all investigated; the second part of the study lasted for 12 months and two tanks with treatments NS and NF were investigated. Dynamic flux chambers and a photoacoustic gas analyzer were used to measure ammonia emission rates.

There was no significant change of the N content of manure as the dietary N content is reduced (from 17.8% to 15.9% crude protein). However, ammonia emission rates from manure storage tanks were reduced by 33% (from 27.4 $\pm$38.1 to 18.4 $\pm$21.9 mg m^{-2} h^{-1}; P<0.0001 based on paired t-test). Flushing manure reduced emission rates by 72% compared to scraping manure (from 35.6 $\pm$39.6 to 10.1 $\pm$8.2 mg m^{-2} h^{-1}; P<0.0001 based on paired t-test). Ammonia emission rates for NS, NF, LS and LF were 43.9 $\pm$48.0, 10.9 $\pm$8.7, 27.4 $\pm$27.3, and 9.3 $\pm$7.8 mg m^{-2} h^{-1}, respectively. The chamber headspace temperature for NS, NF, LS and LF were 26.0 ± 6.9, 25.8 ± 6.8, 26.6 ± 6.5, and 27.2 ± 6.7 ℃, respectively. The manure pH for NS, NF, LS, and LF were 6.3 ± 0.1, 6.4 ± 0.3, 6.4 ± 0.1, and 6.1 ± 0.1, respectively. Both dietary N reduction and manure flushing are recommended to reduce ammonia emission rates from dairy manure storage tanks.

Ammonia emission rates were higher in summer and fall, due to higher air temperature and higher manure pH. The pH of scraped manure was 7.2±0.6, 6.7±0.2, 6.5±0.3 and 7.0±0.3 for fall, winter, spring and summer, respectively. The pH of flushed manure was 6.8±0.4, 6.7±0.4, 6.4±0.3 and 6.8±0.4 for fall, winter, spring and summer, respectively. Ammonia emission rates from scraped manure for fall, winter, spring, and summer were 7.4 ± 8.6, -0.5 ± 1.2, 1.1 ± 1.9, and 5.8 ± 2.7 mg m^{-2} h^{-1}, respectively. Ammonia emission rates from flushed manure for fall, winter, spring, and summer were 3.9 ± 4.2, -0.5 ± 0.9, 0.8 ± 1.4, and 4.4 ± 1.2 mg m^{-2} h^{-1}, respectively. Seasonal changes of air temperature and manure pH were key factors affecting ammonia emissions from manure storage in this study. Seasonal climate conditions including precipitations (rainstorms and snows) and icing can cause reduction of ammonia emissions from manure storage in open air. More attention should be paid to reduce ammonia emissions in warmer seasons, e.g., by covering the storage facilities.

Keywords: ammonia emissions, dairy cow, dietary N, manure removal, seasonal change

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NOMENCLATURE

AFO – Animal Feeding Operation

COD – Chemical Oxygen Demand

CP – Crude Protein

RDP – Ruminally Degradable Protein

RUP – Ruminally Undegradable Protein

TAN – Total Ammoniacal Nitrogen

TKN – Total Kjeldahl Nitrogen

TP – Total Phosphorus

TS – Total Solids

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Chapter 1. Introduction

1.1 General background

In the United States, ammonia emissions from animal feeding operations (AFOs) are 2.4×10^6 tons nitrogen (N) yr^{-1} (in 2002), accounting for 55% of total ammonia emissions (Aneja *et al.*, 2008). In Europe and Canada, ammonia emissions from AFOs (in 2007) accounted for 70% and 66% of total ammonia emissions, respectively (EMEP, 2009).

In all animal types, dairy cattle is the largest source of ammonia in the U.S., accounting for 23% of ammonia emissions from AFOs (USEPA, 2004). There are approximately 9 million dairy cattle in the U.S. (USDA-NASS, 2008), which are either heifer, lactating or dry. A lactating dairy cow has an average live weight of approximately 600 kg (USEPA, 2004), producing an average of 69 kg manure (urine and feces) per day (ASABE, 2005). A dairy cow emits 13.1~55.5 (23.9 on average) kg NH_3 y^{-1} (Pinder *et al.*, 2004).

The major concern on ammonia at the local level is the ambient ammonia concentration, because most air quality issues, health issues, and odor complaints are related to the concentration of ammonia. Near some AFOs (within 100 m), the long-term mean concentration of ammonia can reach up to 0.11 ppm, while in some rural areas it is only 0.0002 to 0.02 ppm (Davison and Cape, 2003).

1.2 Ammonia production and emissions from dairy operations

1.2.1 Ammonia production

Ammonia is a product of a series of microbial and chemical reactions from either fresh or stored dairy manure (urine and feces). The ammonia emitted from dairy manure originates from the unconverted dietary N. The N in a cow's diet is mainly in the form of different proteins, and only approximately 57% of the dietary N is available to the rumen microbes (Kebreab *et al.*, 2002). The diet for dairy cattle must satisfy requirements for growth, maintenance, and milk production. For lactating cows, the net N gain for body growth and maintenance is small, and the N intake from diet is mostly partitioned in the milk, urine, and feces. One of the most important parameters for the diet quality is the N content (%N), which includes protein N (dominant) and non-protein N. Instead of directly using %N, crude protein content (%CP) is usually used in dairy science research, which can be assumed equal to %N×6.25.

Cyriac *et al.* (2008) reported that reducing ruminally degradable protein (RDP) in diet for mid-lactating cows from 9.5-10.5%, as suggested by NRC (2001), to 8.8% (15.9% CP) successfully improved N utilization efficiency without affecting milk quantity and quality. Further reduction of dietary N reduced the milk quality. Both the CP% and the protein composition are important for the N absorption by cows (Christensen *et al.*, 1993). Feed intake, dietary CP content, stage and level of lactation, availability of the nutrients and animal size affect the N excretion rate (ASABE, 2005; Sutton *et al.*, 2001). The estimated N excretion rate is reported by ASABE (2005) as 0.45 kg cow^{-1} d^{-1}, or by other sources as 0.17-0.47 kg cow^{-1} d^{-1} (MWPS, 1985; Tomlinson *et al.*, 1996; Vanhorn *et al.*, 1994).

Ammonia production (or N mineralization) in dairy manure is actually the microbial degradation of the nitrogenous compounds in urine and feces (Table 1-1).

Table 1-1. Ammonia production from dairy manure (Anderson *et al.*, 1987; Mobley and Hausinger, 1989)

	Short-term	**Long-term**
Mechanism	Degradation (hydrolysis) of urea in urine	Degradation of undigested proteins and other nitrogenous compounds in feces
Reaction rate	Fast (several minutes to hours)	Slow (several days to months)
Reaction equation	(Equation 1.1)	(Equation 1.2)

Primarily, ammonia is produced from urea ($CO(NH_2)_2$) hydrolysis, which is accelerated with the presence of urease enzymes. Most urea exists in urine and most urease enzymes exist in feces. Therefore, when urine and feces mix, the ammonia production is enhanced (Muck, 1982). In manure storage, most urea N can be degraded in one week (Külling *et al.*, 2001; Whitehead and Raistrick, 1993). The degradation of urea in urine can be expressed by the equation below (Mobley and Hausinger, 1989):

$$\mathrm{CO(NH_2)_2 + H_2O \xrightarrow{Urease} 2NH_3 + CO_2} \qquad (1\text{-}1)$$

Secondarily, ammonia can also be produced from degradation of undigested proteins and other nitrogenous compounds in feces, but this process is much slower than urea degradation. Although various reactions can be included in this process, the equation by Anderson *et al.* (1987) to model degradation of organic compounds in swine manure tanks can be used for dairy feces:

$$\mathrm{C_nH_aO_bN_cS_g} + \left(2\mathrm{n} - \mathrm{b} - \frac{\mathrm{de}}{4} - 2\frac{\mathrm{df}}{5}\right)\mathrm{H_2O} = \left(\mathrm{n} - \frac{\mathrm{de}}{8} - \frac{\mathrm{df}}{4}\right)\mathrm{CO_2} + \left(\frac{\mathrm{de}}{8}\right)\mathrm{CH_4} + \left(\mathrm{c} - \frac{\mathrm{df}}{20}\right)\mathrm{NH_3} + \mathrm{gH_2S} + \left(\frac{\mathrm{df}}{20}\right)\mathrm{C_5H_7O_5N} \qquad (1\text{-}2)$$

where

$C_nH_aO_bN_cS_g$ = empirical formulation for the degradable portion of the wastes

$C_5H_7O_2N$ = composition of microbial cells

d = 4n+a-2b-3c-g

e = fraction of waste chemical oxygen demand (COD) converted to methane gas for energy

f = fraction of waste COD synthesized into cells

On dairy barn floors, since the manure is flushed several times a day, the ammonia production is mostly from urea degradation. In the dairy manure storage, the two degradation processes mentioned above may coexist, but the decomposition of non-urea organic N (undigested proteins in feces) is considered very low, because the anaerobic digestion conditions such as mixing and temperature are not optimized in typical manure storage (Muck and Steenhuis, 1982).

1.2.2 Ammonia chemistry

Ammonia is a colorless alkaline gas at room temperature and standard atmospheric pressure (20 ℃, 1.01×10^5 Pa), with the molecular weight of 17 g $mole^{-1}$. In water solution or liquid manure, ammonia can exist in different forms including NH_3 and NH_4^+. Under alkaline conditions, NH_3 is favorable, so ammonia emissions from the manure is high; under acidic conditions, NH_4^+ (ammonium ion) is favorable, so the ammonia loss from the manure is low (Hartung and Phillips, 1994). NH_3 and NH_4^+ are balanced through the dissociation equilibrium (Seinfeld and Pandis, 2006. p299; Zhang *et al.*, 1994):

$$\mathrm{NH_4^+} \leftrightarrow \mathrm{NH_3} + \mathrm{H^+} \tag{1-3}$$

The dissociation constant K_d for this equilibrium changes with temperature (Jayaweera and Mikkelsen, 1990):

$$K_d = \frac{[NH_3][H^+]}{[NH_4^+]} = 10^{-(0.0897+\frac{2729}{T})} \quad (1\text{-}4)$$

where

K_d = dissociation constant of NH_4^+ based on concentration

T = Temperature, K

Ammonia dissociation and release from both dairy barn floors and manure storage is affected by manure pH (Beegle *et al.*, 2008; Muck and Steenhuis, 1981; Muck and Steenhuis, 1982). The fraction (F) of free ammonia N in TAN is usually reported as a function of pH and temperature (Zhang *et al.*, 1994):

$$F = \frac{[NH_{3(aq)}]}{[TAN]} = \frac{K_d \cdot 10^{pH}}{K_d \cdot 10^{pH} + 1} \quad (1\text{-}5)$$

where

F = fraction of $NH_{3(aq)}$ in TAN, %

$[NH_{3(aq)}]$ = ammonia concentration in the liquid, mg L^{-1}

[TAN] = Total Ammoniacal N, mg L^{-1}

The dependence of F on pH and temperature is also shown in Figure 1-1. The pH of dairy manure can vary widely, depending on the floor conditions, storage conditions, dilution, etc.

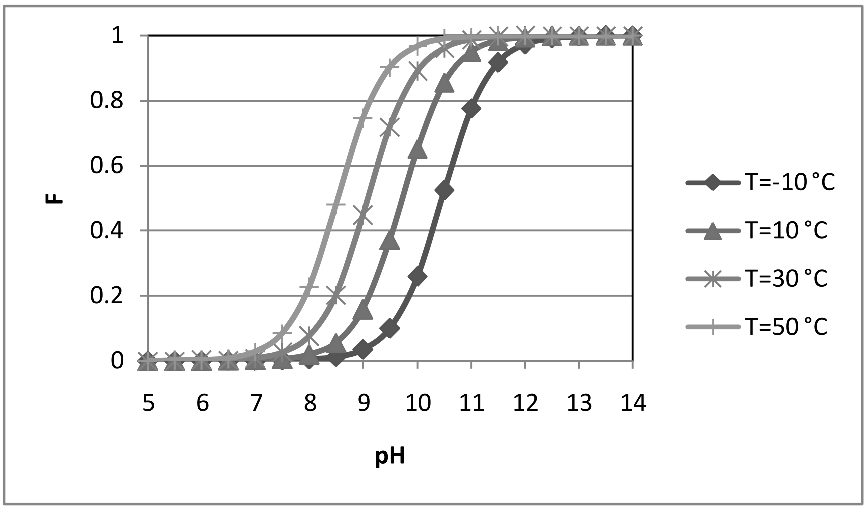

Figure 1-1. Fraction of NH_3 in TAN vs. pH at different temperatures

(adapted from Jayaweera and Mikkelsen, 1990)

In concentrated liquid system like manure storage, the high ionic strength makes the active concentration (i.e., activity) smaller than the analytical concentration (Arogo *et al.*, 2003). Therefore, using TAN and K_d mentioned above may cause inaccurate estimation of ammonia emission rates. Arogo *et al.* (2003) suggested using following equations to calculate an adjusted K_d' for swine waste storage based on activity:

$$K_d' = \frac{\gamma_{NH_3}[NH_{3(aq)}]\gamma_{H^+}[H^+]}{\gamma_{NH_4^+}[NH_4^+]} \quad (1\text{-}6)$$

$$\log(\gamma) = \sum_{i=1}^{s} v_i \log(\gamma_i) = -\sum_{i=1}^{s} v_i A z_i^2 \sqrt{I} \quad (1\text{-}7)$$

$$I = 2.5 \times 10^{-5} \times TDS \quad (1\text{-}8)$$

where

K_d' = adjusted dissociation constant of NH_4^+ based on activity

γ = activity coefficient

I = ionic strength

z_i = the charge number of ion species i

A = a constant depending on the solvent

s = the number of species participating in the reaction

ν_i = the stoichiometric coefficient of species i

TDS = total dissolved solids, %

1.2.3 Ammonia diffusion

In liquid manure storage which is not aerated or stirred, the ammonia concentration gradient is the major driving force and diffusion is major mechanism for ammonia mass transfer in liquid (Muck and Steenhuis, 1982). One-dimensional (vertical direction) molecular diffusion mechanism was usually considered in previous studies, which is governed by Fick's first law and second law (Zhang *et al.*, 1994):

$$J_z = -D_{AB}\left(\frac{dC_A}{dz}\right) \tag{1-9}$$

$$\frac{\partial C_A}{\partial t} = D_{AB}\left(\frac{\partial^2 C_A}{\partial z^2}\right) + R_A(z,t) \tag{1-10}$$

where

J_z = mass flux in z direction, kg m^{-2} s^{-1}

dC_A/dz = concentration gradient of solute A (NH_3) in z direction, kg m^{-3} m^{-1}

D_{AB} = diffusivity of solute A (NH_3) in solvent B (H_2O), m^2 s^{-1}

R_A = generation rate of solute A (NH_3), kg m^{-3} s^{-1}

1.2.4 Ammonia volatilization

Ammonia is volatilized from liquid phase to gaseous phase, from the surface of manure on dairy barn floors or the surface of liquid manure storage. The liquid-gas ammonia equilibrium at the manure interface follows Henry's law (adapted from Zhang *et al.*, 1994):

$$[NH_{3(g)}] = K_H\{NH_{3(aq)}\} \tag{1-11}$$

Where

$[NH_{3(g)}]$ = Concentration of ammonia in gaseous phase, mg L^{-1}

K_H = Henry's Constant for ammonia (dimensionless)

$\{NH_{3(aq)}\}$ = Activity of ammonia in aqueous phase, mg L^{-1}

The volatilization process of ammonia from animal manure is most commonly estimated using the Two-Film Theory (Lewis and Whitman, 1924). Ammonia emissions are driven by the concentration gradient between liquid manure and air. The N loss in ammonia emissions from manure can be proportional to manure TAN (Hutchings *et al.*, 1996), or expressed as a percentage of manure TAN or TKN content. Misselbrook *et al.* (2005b) reported ammonia emissions from manure storage in two weeks as 24 and 31% of manure TAN for low and high CP diets, respectively. Dinuccio *et al.* (2008) reported that after 30 days of storage, ammonia emissions from non-treated cattle manure slurries accounted for 3.60±0.09% and 16.5±0.17% of the TKN at 5 and 25 ˚C, respectively. Powell *et al.* (2008) reported that ammonia N emissions accounted for approximately 4 to 7% of consumed feed N, 4 to 10% of manure TKN, and 9 to 20% of manure TAN. Manure N content is mainly determined by the dietary N and livestock metabolism as discussed in Section 1.2.1.

Ammonia emission rates from animal manure increase with air velocity, although the relationship is not necessarily linear (Olesen and Sommer, 1993; Ro *et al.*, 2008). However, Zhang *et al.* (1994) reported that high air velocity enhances ammonia emission rates only for a certain aqueous ammonia concentration, but with higher velocity, ammonia emission rates initially increased but later decreased (because the surface aqueous ammonia concentration decreased and the process became limited by the diffusion rate below the surface).

Based on the descriptions above, a nitrogen flowchart in typical dairy farms for lactating cows is made, as shown in Figure 1-2.

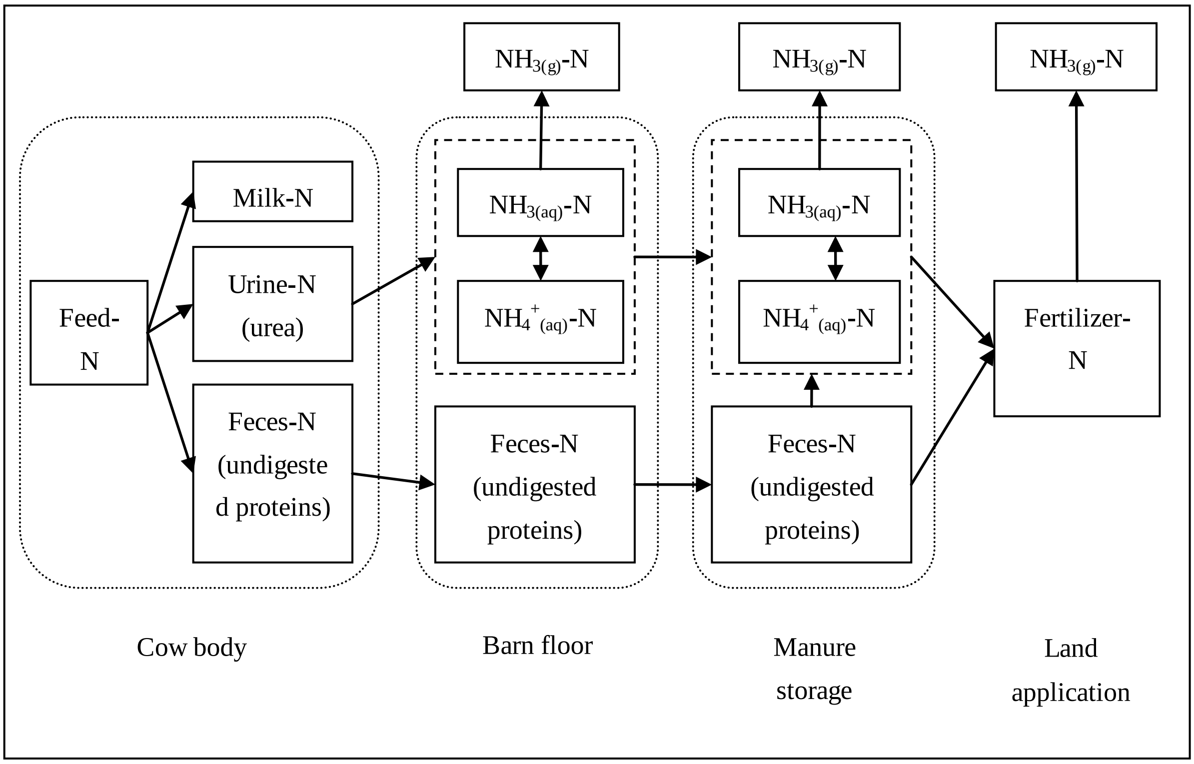

Figure 1-2. Nitrogen flowchart in typical dairy farms with lactating cows

1.2.5 Effects of ammonia emissions

1.2.5.1 Environmental effects

NH_3 in air can ionize to ammonium ion (NH_4^+) and react with acidic species to form fine particulate matter ($PM_{2.5}$, aerodynamic diameter equal to or smaller than 2.5 μm):

$$NH_3 + H^+ \rightarrow NH_4^+ \tag{1-12}$$

$$NH_4^+ + NO_3^- \rightarrow NH_4NO_3 \tag{1-13}$$

$$NH_4^+ + SO_4^{2-} \rightarrow (NH_4)_2SO_4 \tag{1-14}$$

This $PM_{2.5}$ contributes to the regional haze, low visibility, radiative forcing and global climate change (Erisman and Monteny, 1998; Gates *et al.*, 2005; McCubbin *et al.*, 2002), and may impair the health of human beings (Popendorf *et al.*, 1985) and animals (Macvean *et al.*, 1986) at high concentrations. McCubbin *et al.* (2002) estimated that reducing ammonia emissions from AFOs by 10% could save more than \$4 billion year^{-1} on health issues related to PM.

Eventually most ammonia in the atmosphere returns to land and water systems. Ammonia deposited on land can cause acidification of soil (by nitrification and leaching), and the increased soil N content may reduce species diversity in natural ecosystems (Sutton *et al.*, 1993; Todd *et al.*, 2004). Ammonia deposited directly from atmosphere into water or indirectly from soil into the water system can further raise the N content in water and cause eutrophication problems (Hartung and Phillips, 1994).

Ammonia is a source of odor, which can be detected by human nose above 0.017 ppm, and recognized as ammonia above 37 ppm (Hamilton and Arogo, 1999). Ammonia is a nuisance to farm workers and a source of complaints from nearby residents when the concentration is high, but the ammonia concentrations in the air at or near AFOs are usually lower than the permissible levels for human health. The permissible level of human exposure to ammonia is defined by the Time-Weighted Average (TWA; continuous exposure for 8 h) as 25 ppm, the Short-Term Exposure Limit (STEL; 15 minutes exposure) as 35 ppm, and the concentration Immediately Dangerous to Life or Health (IDLH; 30 minutes exposure) as 500 ppm (Issley and Lang, 2007). MWPS (1985) reported that 25-30 ppm is the lowest level for ammonia to cause a burning sensation to the eyes in humans. In comparison, Davison and Cape (2003) reported that long-term mean concentrations of ammonia near some AFOs (within 100 m) were only up to 0.11 ppm, although it is higher than in some rural areas (0.0002 to 0.02 ppm). Exposure of dairy cows to ammonia at high concentrations (>200 ppm) or for a long time may cause sneezing, appetite loss, and even respiratory tract diseases to animals (MWPS, 1985), but there are no known reports about effects of ammonia exposure on the milk production of dairy cows.

1.2.5.2 Loss of fertilizer value

Dairy manure can be used as fertilizer (Muck and Steenhuis, 1981; Paul *et al.*, 1998). Therefore, ammonia loss to the atmosphere means loss of fertilizer value in manure (Hartung and Phillips, 1994; Muck and Steenhuis, 1982). Reducing ammonia emissions and keeping more N in manure will benefit the nutrient content of manure as a fertilizer.

1.2.6 Mitigation of ammonia emissions

Nitrogen cycling is necessary for livestock industries to maximize N utilization efficiency, maximized recycling of manure nutrients, and minimize N loss as ammonia or in water runoff. A comprehensive plan to advance the best management practices (BMPs) is required to optimize the system in nutrient management. Mitigation of ammonia emissions from dairy farms can benefit the farmers and the environment in several ways: (1) protect the health of dairy cattle, workers and nearby residents; (2) help the dairy farms not exceed potential regulatory limits in future on air quality; and (3) maintain the N content in manure for fertilizer use.

1.2.6.1 Technologies to mitigate ammonia emissions

Mitigation of ammonia emissions can be achieved by two strategies: reduction and remediation. The reduction strategy refers to reducing the released N from the source (e.g., total animal numbers, dietary N reduction). The remediation strategy does not change the total N released from the system, but only reduces NH_3 emissions, e.g., by manure storage covering (Hartung and Phillips, 1994) or by using chemical additives to manure. Sometimes, the remediation strategy can only reduce NH_3 emissions during a certain period or in a certain place, e.g., by house ventilation or more frequent manure removal from floor. Therefore, the reduction strategy is introduced below with emphasis.

Reducing dietary crude protein (CP) for dairy cows can reduce ammonia emissions, but the effects and sides effects of this approach are not consistently concluded. Some researchers reported that both excreted N and ammonia emissions were successfully reduced (de Boer *et al.*, 2002; Jackson *et al.*, 2006; Monteny *et al.*, 2002), others report that ammonia emissions were reduced due to both reduced total excreted N and reduced fraction of urinary N (Külling *et al.*, 2001), yet another found that only excreted N was reduced (Misselbrook *et al.*, 2005b). Further, some researchers reported that milk production was reduced (Burgos *et al.*, 2006; Frank and Swensson, 2002).

Some other techniques involved changes in the feeding, which can also reduce N excretion and ammonia emissions from manure. For instance, precision feeding techniques can provide feeds that will meet nutrient requirements and minimize excretion, while phase feeding can meet the needs of lactating cow at different stages of lactation, thereby reducing nutrient excretion (Sutton *et al.*, 2001).

1.2.6.2 Laws and regulations related to ammonia emissions

In the United States, the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) may require farms with ammonia emissions above 45 kg d^{-1} to report to an authoritative agency (Gates *et al.*, 2005), so as to provide the government and public a knowledge of potential risks. A permit is needed if a farm site exceeds Clean Air Act (CAA) limits of 100 ton y^{-1} $PM_{2.5}$ (Gates *et al.*, 2005), which are partly due to ammonia as discussed in Section 1.2.5.1. The concentration of $PM_{2.5}$ is also regulated to 15.0 μg m^{-3} for annual standard or 35.0 μg m^{-3} for 24-hour standard, by National Ambient Air Quality Standards, or NAAQS (USEPA, 2006).

USEPA established a National Air Emissions Monitoring Study (NAEMS) in 2006 with Agricultural Air Research Council and organizations representing various livestock industries, in order to obtain more complete and long-term data about air pollutant emissions (including ammonia) from AFOs (Purdue University, 2006). This study will benefit future policies to control ammonia emissions.

USEPA also included controlling runoff of manure nutrients from the largest AFOs in Clean Water Act (CWA) regulations in 2003, which later caused 49% of dairy production to be operated under Certified Nutrient Management Plans, or CNMPs (MacDonald and McBride, 2009). These regulations are related to ammonia emission control, because (1) ammonia in the atmosphere can deposit back to the land as a nutrient; and (2) one of the most common ammonia reduction strategies, dietary N reduction, can also help to reduce nutrient runoff from manure.

1.2.7 Manure removal practices and ammonia emissions

Manure scraping and flushing are commonly used to remove manure from dairy barns in the U.S. (USDA, 1996). Manure scraping may reduce ammonia emissions when manure is removed frequently, but may also enhance ammonia emissions because the urine puddles have thinner thickness and larger surface area (Braam *et al.*, 1997). Manure flushing is more beneficial in reducing ammonia emissions from dairy barn floors as compared to manure scraping, due to the dilution and removal of urine on floors (Kroodsma *et al.*, 1993). More frequent flushing can cause more ammonia reduction because cow urination is frequent and urea degradation is fast (Kroodsma *et al.*, 1993). One problem for manure flushing is that when the temperature is below 0 ℃, flushing needs to be suspended to avoid floor icing (Johnson *et al.*, 1989). Another problem is the large volume of liquid manure when flushing is frequently conducted (Kroodsma *et al.*, 1993), which requires large storage capacity. Some dairy farms reuse part of manure tank liquid to flush barn floors, because this saves the cost of using clean water. The reused shred liquid contains ammonia, which may introduce a new source of ammonia emissions when flushing. However, overall ammonia emissions from barn floors can still be reduced as the manure is flushed away several times a day.

1.2.8 Manure storage and ammonia emissions

Two common facilities for dairy manure storage are above-ground tanks and earthen basins, usually built in concrete confinement (Sommer *et al.*, 2006). Compared to earthen basins, above-ground tanks are easier to build and may cause lower ammonia emissions because they usually have smaller surface area (Muck and Steenhuis, 1982).

Manure dilution ratio affects ammonia emission rates from the manure storage, because more diluted manure has lower TKN and TAN concentrations, and the ammonia production rate is driven by the gradient between ammonia concentration in the liquid and in the air.

Non-treated manure in storage is mostly under anaerobic conditions, even if the surface of the manure is open to air. Therefore, nitrification and denitrification are not significant. In addition, the anaerobic decomposition of organic N into NH_4^+ and NH_3 is slow because the conditions such as mixing and temperature are not optimal (Muck and Steenhuis, 1982). Interruption of the anaerobic condition (by aeration or stirring) is not recommended for manure storage facilities. Aeration can cause nitrification and denitrification, and is only used when removal of extra N is needed. Intermittent or periodic stirring of the manure may increase ammonia losses, because stirring accelerates microbial activity, mineralization and diffusion of N (Gilbertson *et al.*, 1981; Sparks, 2008). It was reported by Amon *et al.* (2006) that aeration almost doubled ammonia emissions from dairy manure storage.

1.2.8.1 Storage surface area and depth

The capacity of manure storage is usually calculated by daily manure production rate, and land application frequency and quantity, with extra capacity for storm events considered. After the storage capacity is determined, the ratio of surface area to depth also needs to be designed. Smaller surface area causes less use of land area and lower ammonia emissions (Muck and Steenhuis, 1982). Sievers *et al.* (2000) reported that for swine waste lagoons, larger surface area to depth ratios caused the ammonia N concentration in liquid decrease faster, which means higher ammonia emissions occurred. However, reduced storage surface area also means increased depth. For earthen basins, increased depth may cause higher cost to pump out manure onto ground.

Muck and Steenhuis (1982) suggested that a smaller surface area to depth ratio means higher "loading rate" or the added depth per day (cm d^{-1}) for a particular farm, where the daily manure production rate is constant. They further reported that ammonia emission rate decreases as the loading rate increases, because the average distance that NH_3-N needs to diffuse to surface is longer. Above-ground tanks usually have smaller surface area or higher depth than earthen storage, and thus have benefits in terms of N conservation (Muck and Steenhuis, 1982).

1.2.8.2 Storage time

The timing and frequency of manure removal from storage facility depends on the crop requirements, which vary considerably in different climates, locations and even farms. The common interval is no longer than six months (MWPS, 1985), but more likely the manure is not removed at equal intervals in a year. A longer removal interval implies a larger storage capacity, but the effect of the manure storage time on ammonia emissions is not clear. Muck and Steenhuis (1982) estimated using a model that after 20 days of manure loading (from top), the ammonia emission rate becomes steady (for all three temperatures, 10, 20 and 30 ℃).

1.2.8.3 Covered / uncovered storage

Storage covering is a useful strategy to enhance anaerobic conditions and significantly reduce (up to 90 %) ammonia emissions from storage (Arogo *et al.*, 2006; Hartung and Phillips, 1994). Gilbertson *et al.* (1981) also reported that ammonia emission rates from closed containers are much lower than from open containers.

1.3 Summary

Ammonia is a pollutant to the environment, including air, land and water systems. To reduce ammonia emissions from dairy operations, different measures were suggested, including dietary N reduction and improved manure management. Dietary N reduction can reduce N excretion and thus reduce ammonia emissions. Manure removal practices affect ammonia emissions from both floors and manure storage facilities (flushing better than scraping). Manure storage conditions (surface area, depth, storage time, and covering) also affect ammonia emissions from storage facilities.

Studies considering effects of both dietary N reduction and manure removal and storage conditions on ammonia emissions are limited. Only a few studies quantified the effect of dietary N reduction on ammonia emissions from manure storage (James *et al.*, 1999; Külling *et al.*, 2001; Paul *et al.*, 1998). Most experimental studies dealing with manure storage used one-time manure addition, for which ammonia emission rates would decrease exponentially with time (Külling *et al.*, 2001). Further, many previous studies were conducted in controlled environment (e.g., controlled temperature; indoor environment without rainfall or other seasonal events), which were helpful to discern treatment effects but not describing the real environment. Additional research is needed to understand effects of diets and manure removal practices on ammonia emissions from manure storage under natural conditions.

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Chapter 2. Ammonia Emissions from Dairy Manure Storage Tanks Affected by Diets and Manure Removal Practices

2.1 Abstract

The objectives of this study were to determine: 1) ammonia emission rates from stored scraped and flushed manure from dairy cows fed either normal or low N diet; and 2) seasonal effects on ammonia emission rates from stored scraped and flushed dairy manure. Four pilot-scale tanks were used for manure storage with different treatments - scraped manure for normal diet (NS), flushed manure for normal diet (NF), scraped manure for low N diet (LS), and flushed manure for low N diet (LF). The first part of the study lasted for 1 month and four treatments were all investigated; the second part of the study lasted for 12 months and two tanks with treatments NS and NF were investigated. Dynamic flux chambers and a photoacoustic gas analyzer were used to measure ammonia emission rates.

There was no significant change of the N content of manure as the dietary N content is reduced (from 17.8% to 15.9% crude protein). However, ammonia emission rates from manure storage tanks were reduced by 33% (from 27.4 ± 38.1 to 18.4 ± 21.9 mg m^{-2} h^{-1}; P<0.0001 based on paired t-test). Flushing manure reduced emission rates by 72% compared to scraping manure (from 35.6 ± 39.6 to 10.1 ± 8.2 mg m^{-2} h^{-1}; P<0.0001 based on paired t-test). Ammonia emission rates for NS, NF, LS and LF were 43.9 ± 48.0, 10.9 ± 8.7, 27.4 ± 27.3, and 9.3 ± 7.8 mg m^{-2} h^{-1}, respectively. The chamber headspace temperature for NS, NF, LS and LF were 26.0 ± 6.9, 25.8 ± 6.8, 26.6 ± 6.5, and 27.2 ± 6.7 ℃, respectively. The manure pH for NS, NF, LS, and LF were 6.3 ± 0.1, 6.4 ± 0.3, 6.4 ± 0.1, and

6.1 ± 0.1, respectively. Both dietary N reduction and manure flushing are recommended to reduce ammonia emission rates from dairy manure storage tanks.

Ammonia emission rates were higher in summer and fall, due to higher air temperature and higher manure pH. The pH of scraped manure was 7.2 ±0.6, 6.7 ±0.2, 6.5 ±0.3 and 7.0 ±0.3 for fall, winter, spring and summer, respectively. The pH of flushed manure was 6.8 ±0.4, 6.7 ±0.4, 6.4 ±0.3 and 6.8 ±0.4 for fall, winter, spring and summer, respectively. Ammonia emission rates from scraped manure for fall, winter, spring, and summer were 7.4 ± 8.6, -0.5 ± 1.2, 1.1 ± 1.9, and 5.8 ± 2.7 mg m^{-2} h^{-1}, respectively. Ammonia emission rates from flushed manure for fall, winter, spring, and summer were 3.9 ± 4.2, -0.5 ± 0.9, 0.8 ± 1.4, and 4.4 ± 1.2 mg m^{-2} h^{-1}, respectively. Seasonal changes of air temperature and manure pH were key factors affecting ammonia emissions from manure storage in this study. Seasonal climate conditions including precipitations (rainstorms and snows) and icing can cause reduction of ammonia emissions from manure storage in open air. More attention should be paid to reduce ammonia emissions in warmer seasons, e.g., by covering the storage facilities.

Keywords: ammonia emissions, dairy cow, dietary N, manure removal, seasonal change

2.2 Introduction

Ammonia (NH_3) emission is a potential pollution problem for animal feeding operations (AFOs). Ammonia is a precursor to fine particulate matter ($PM_{2.5}$, aerodynamic diameter equal to or smaller than 2.5 μm), which may contribute to the formation of regional haze and low visibility (Erisman and Monteny, 1998; McCubbin *et al.*, 2002). Ammonia may also deposit from the air onto land and into water systems (e.g., by raining). The deposition can reduce ammonia in the air, but may cause eutrophication in water systems and increased nitrogen (N) content in soil, and reduce the species diversity in ecosystems (Sutton *et al.*, 1993; Todd *et al.*, 2004). Ammonia may impair the health of human beings and animals when the concentration is high (Issley and Lang, 2007; MWPS, 1985). Ammonia loss to the atmosphere means loss of fertilizer value in manure (Hartung and Phillips, 1994; Muck and Steenhuis, 1982).

In the United States, ammonia emissions from AFOs are 2.4×10^6 tons N yr^{-1}, accounting for 55% of the total emissions (Aneja *et al.*, 2008). In all animal types, dairy cattle is the largest source of ammonia, accounting for 23% of emissions from AFOs (USEPA, 2004). A dairy cow emits 13.1~55.5 (23.9 on average) kg NH_3 y^{-1} (Pinder *et al.*, 2004). Therefore, the dairy industry is gaining more attention from both local and national governments (USEPA, 2004).

In most dairy operations, manure is stored in above-ground tanks or earthen basins till it is applied in land for crops or pasture (Muck and Steenhuis, 1982). Ammonia emission rates from dairy manure storage can range from 0 to 540 mg m^{-2} h^{-1} (Amon *et al.*, 2006; Rumburg *et al.*, 2008). There are usually temporal effects on ammonia emission rates from manure storage, which are due to the diurnal and seasonal change of air temperature and other climate conditions (e.g., precipitation and icing).

Several measures can be used to reduce ammonia emissions as listed below, but each measure has its limitations. The emissions can be reduced by natural surface crusting (Külling *et al.*, 2001; Misselbrook *et al.*, 2005a; Smith *et al.*, 2007), but this method is not applicable for flushed manure or in rainy conditions. Ammonia emissions can also be reduced (up to 90%) by covering the storage facility (Arogo *et al.*, 2006; Hartung and Phillips, 1994), but it is not commonly applied in dairy farms because it can be expensive and labor-intensive. Mechanical liquid-solids separation before liquid manure storage cannot reduce ammonia emissions from the liquid manure storage (Dinuccio *et al.*, 2008). Therefore, these above-mentioned measures are not considered in this study.

Reducing dietary crude protein (CP) for dairy cows can reduce ammonia emissions, but the effects and sides effects of this approach are not consistently concluded. Some researchers reported that both excreted N and ammonia emissions were successfully reduced (de Boer *et al.*, 2002; Jackson *et al.*, 2006; Monteny *et al.*, 2002), others report that ammonia emissions were reduced due to both reduced total excreted N and reduced fraction of urinary N (Külling *et al.*, 2001), yet another found that only excreted N was reduced (Misselbrook *et al.*, 2005b). Further, some researchers reported that milk production was reduced (Burgos *et al.*, 2006; Frank and Swensson, 2002).

Most studies on dietary N reduction focused on ammonia emissions from manure in simulated lab environment, on barn floors or for the whole system of dairy operation, while only a few studies quantified the effect of dietary N reduction on ammonia emissions from manure storage (James *et al.*, 1999; Külling *et al.*, 2001; Paul *et al.*, 1998).

The manure removal practices are important to ammonia emissions from manure storage.

Manure on solid floor or other facilities are typically removed into storage by scraping or flushing. Flushing reduces ammonia emissions in two ways. First, flushing reduces ammonia emissions from barn floors, because the urine on floors is diluted and partly removed (Kroodsma *et al.*, 1993), and urea N in urine is a major source of ammonia (Muck, 1982). Second, flushing reduces ammonia emissions from manure storage, because the manure is diluted and the ammonia concentration in manure is reduced, and ammonia emissions are driven by the concentration gradient between liquid manure and air. However, previous studies have not investigated the combined effects of flushing with dietary N reduction. Further, most experimental studies dealing with manure storage used one-time manure addition, for which ammonia emission rates would decrease exponentially with time (Külling *et al.*, 2001).

Seasonal environmental factors affect ammonia emissions from animal manure. Ammonia emission rates increase with air temperature (Harper *et al.*, 2000; Ni, 1999; Sommer *et al.*, 1991) and air velocity (Olesen and Sommer, 1993; Ro *et al.*, 2008), and decrease with rainfall events (Sommer and Olesen, 2000; Westerman *et al.*, 2006). Many previous studies were conducted in controlled environment (e.g., controlled temperature; indoor environment without rainfall or other seasonal events), which were helpful to discern treatment effects but not describing the real environment.

A series of studies were conducted to determine how changes in dietary N affect ammonia emissions from dairy barn floors and manure storage. Cyriac *et al.* (2008) reported that reducing diet ruminally degradable protein (RDP) for mid-lactating cows from 9.5-10.5%, as suggested by NRC (2001), to 8.8% (15.9% CP) successfully improved N utilization efficiency without affecting milk quantity and quality. Further reduction of dietary N reduced the milk quality. Sparks (2008) found that dietary N reduction resulted in lower TKN in excretion, and the average ammonia emission rate for scraped manure was significantly larger (4.6 $\pm$ 2.0 times) than that for flushed manure if both temperature effects and diet effects are removed. Li *et al.* (2009) further showed that the dietary N reduction caused reduction of TKN in excretion but not reduction of ammonia emissions from barn floors, because the complicated conditions on barn floors resulted in large variances.

2.3 Objectives

The objectives of this study were to determine:

1) Ammonia emission rates from stored scraped and flushed manure from dairy cows fed either normal or low N diet;
2) Seasonal effects on ammonia emission rates from stored scraped and flushed dairy manure.

2.4 Materials and methods

2.4.1 Objective 1: To determine effects of diets and manure removal practices on ammonia emission rates

2.4.1.1 Diets

This study was conducted at the Virginia Tech Dairy Complex (VTDC), where approximately 200 lactating cows were housed in a free-stall barn. Diets were formulated to meet NRC (2001) recommendations for net energy of lactation, ruminally undegradable protein (RUP), minerals, and vitamins for a mature lactating Holstein cow (70 d in milk) and producing 36.3 kg milk per day. Three concentrate mixes were formulated and blended with the forages to attain high and low N diets (containing 17.8 or 15.9% CP on a dry matter basis, respectively) by adjusting RDP while keeping RUP constant. Cows were fed a total mixed ration once daily at a rate adequate to achieve an average of 10% daily refusals and had free access to fresh water. Cows fed with two diets were located in two different pens, so the manure on floor for each diet can be collected separately. Feeding cows with both diets was started from 07/31/2007.

2.4.1.2 Tank setup, manure collection and addition

Four pilot-scale manure storage tanks (1,136 L each; Rubbermaid Commercial Products Inc., Winchester, VA) were located at an outdoor location in VTDC (Figure 2-1).

Figure 2-1. Manure storage experimental setup showing two tanks with flux chambers

The tanks were setup and labeled according to Table 2-1. Filling of tanks was started one week after starting the diet supply (08/07/2007). The initial feed to the scraped tanks were prepared by adding and mixing 33 L tap water and 68 L scraped manure. The initial feed to the flushed tanks were prepared by adding and mixing 305 L tap water and 68 L scraped manure. Manure was then added into all tanks daily until 09/08/2007, without mixing. Scraped manure was simulated by dumping 0.8 L manure collected from barn floor directly into the tank daily, while flushed manure was simulated by diluting 0.8 L scraped manure with 3.2 L tap water daily to approximate the real ratio. Tap water, rather than treated liquid manure from manure treatment lagoons (as is usually practiced), was used for dilution in order to control the dilution liquid’s contents. Tank weights were measured weekly by a pallet truck with electric scale (Northern Tool & Equipment Co., Burnsville, MN; No. 143168).

Table 2-1. Manure addition to storage tanks

	Tank 1	Tank 2	Tank 3	Tank 4
Diet	normal	normal	low N	low N
Manure removal practice	scraped	flushed	scraped	flushed
Treatment label	NS	NF	LS	LF
Manure added per day	0.8L scraped manure	0.8L scraped manure + 3.2L tap water	0.8L scraped manure	0.8L scraped manure + 3.2L tap water
Period	from 08/07/2007 to 09/03/2008	from 08/07/2007 to 09/03/2008	from 08/07/2007 to 09/08/2007	from 08/07/2007 to 09/08/2007

2.4.1.3 Ammonia emission measurement

Ammonia emissions from the tanks were measured for a period of 1 month from 08/12/2007 to 09/08/2007, using an acrylic dynamic flux chamber with a volume of 49 L (Figure 2-2). The air flow rate through the chamber was 7 L min^{-1}. These specifications were based on an EPA-approved design used to measure emissions at Superfund sites (Eklund, 1992). The chamber floated on the manure surface by plastic foam rings (Figure 2-1). The chamber was secured in the center of tank by connecting three wires from tank edge to a hole on the top of the chamber. Ambient air was pumped (927CA18, Rietschle Thomas Inc., Germany) into the chamber through a mass flow controller (GFC37, Aalborg Inc., NY) and distributed through four holes evenly located along a Teflon tubing inside the chamber. The air mixed with ammonia emitted from manure and was vented through the hole on the top of the chamber. The ammonia concentration (mg m^{-3}) in the chamber was sub-sampled every 5 min and was monitored by a photoacoustic gas analyzer (INNOVA 1312, California Analytical Instruments, Orange, CA). On each measurement day, the ammonia concentration in ambient air was separately measured as background, so that the ammonia concentration in chamber was corrected. Control experiments showed that ammonia losses to the chamber walls were negligible (Sparks, 2008). The constant airflow, although not representative of natural conditions, facilitated the comparison of dietary effects and the study of other environmental factors besides air velocity.

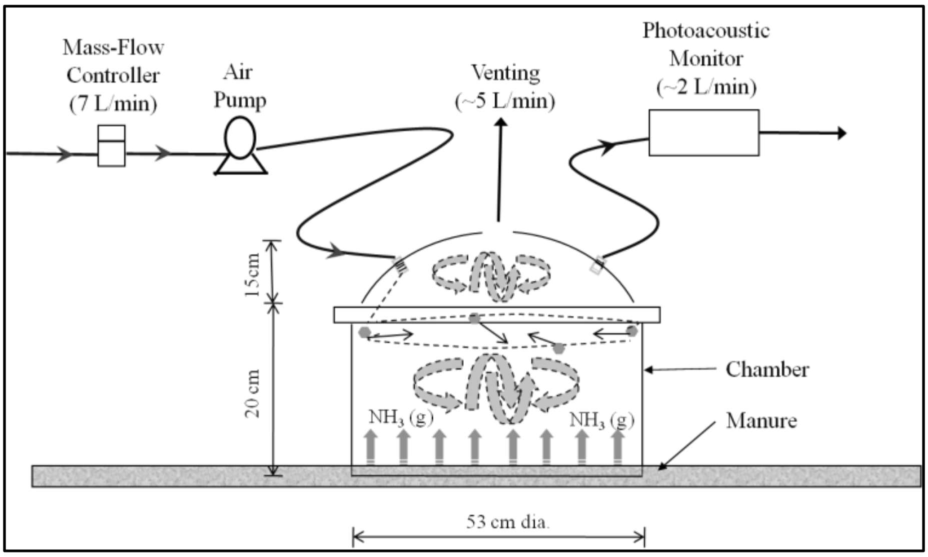

Figure 2-2. Dynamic flux chamber system

Ammonia emissions from four tanks were measured on two consecutive days per week (22 hours d^{-1}) with two tanks per day. Measurement of emissions from four tanks could not be done simultaneously due to equipment limitations. On each measurement day, ammonia emission measurement was conducted once every 2 h starting from 9:25 am. During each 2 h, gas sampling was conducted for the first tank for 1 h, and then switched to the other tank by a programmed switching-valve for another hour, and then switched back for the next 2-h period. During each hour, ammonia emissions were measured at 5-min interval, and the ammonia concentration reached steady state in the last 15 min of the hour. Therefore, only the mean concentration in the last 15 min (3 data points) was used to calculate the emission rate for the 2-h period.

2.4.2 Objective 2: To determine seasonal effects on ammonia emission rates

2.4.2.1 Diets, manure collection, addition and removal

The feeding of low N diet was stopped on 09/09/2007 (the 5th week of measurement) after the end of evaluating Objective 1. The addition of scraped and flushed manure was continued for the normal (control) diet for one year until 09/03/2008, without mixing (Table 2-1). When the tank filled up, it was partly emptied by removing 2/3 of the manure after complete mixing (in real operations the storage is also not completely emptied because the manure quantity is usually larger than cropland requirement). The scraped tank was partly emptied once on 04/20/2008. The flushed tank was partly emptied twice on 01/07/2008 and 04/20/2008.

2.4.2.2 Ammonia emission measurement

The measurement of ammonia emissions from scraped and flushed manure tanks for the normal diet was conducted from 08/12/2007 to 09/03/2008. Ammonia emissions from both tanks were measured on one day for every week (22 hours d^{-1}), with one chamber on each tank. On each measurement day, ammonia emission measurement was conducted once every 2 h starting from 9:25 am. During each 2 h, gas sampling was conducted for the first tank for 1 h, and then switched to the other tank by a programmed switching-valve for another hour, and then switched back for the next 2-h period. During each hour, ammonia emissions were measured at 5-min interval, and the ammonia concentration reached steady state in the last 15 min of the hour. Therefore, only the mean concentration in the last 15 min (3 data points) was used to calculate the emission rate for the 2-h period.

Temperature in each tank was monitored continuously throughout the study by temperature dataloggers (HOBO, Onset Inc., MA), with four sensors collecting temperature for different locations (#1 – chamber headspace, #2 – air above manure, #3 – manure surface, and #4 – approximately 7.6 cm below surface). During non-measurement days when chambers were not placed on manure, the sensor #1 collected the temperature in the air above manure, the same as sensor #2. The experiment location (Blacksburg, Virginia) provided a variety of weather conditions and significant seasonal changes. Tank weights were still measured weekly. Precipitation and air velocity were obtained from a weather station located at the VTDC.

2.4.3 Sample collection and analysis for both objectives

Each week, manure at six random locations in each tank was sampled using a column sampler (good to cover all depth), and was mixed in a bucket. Two 250 mL samples for each tank were taken every week and stored at -18 ℃ before analysis. On each measurement day, manure pH and conductivity at three different locations (three depths for each location: 0, 2.5 and 7.6 cm from surface) in each tank were measured by a pH/ISE/DO meter (ATI Orion, Boston, MA. 5-star).

Manure samples were analyzed for TKN, chemical oxygen demand (COD), total phosphorus (TP), total solids (TS) and alkalinity using APHA (1998) standard methods 4500-N_{org} B, 5220 D, 4500-P B, 2540 B, and 2320, respectively. Manure TAN was tested using a pH/ISE/DO meter (ATI Orion, Boston, MA. 5-star). The concentrations of minerals (K, Na, Ca, Mg, Cu and Zn) were tested by inductively coupled plasma atomic emission spectrometer (ICP) by Virginia Tech Soil Testing Laboratory.

2.4.4 Data analysis for both objectives

2.4.4.1 Ammonia emission rates

The ammonia emission rate (mg m^{-2} h^{-1}) in each 2-h period was calculated by:

$$ER = \frac{(C - C_0) \times Q}{A} \tag{2-1}$$

where

ER = ammonia emission rate (mg m^{-2} h^{-1})

C = ammonia concentration in the flux chamber (mg m^{-3})

C_0 = ammonia concentration in background air (mg m^{-3})

Q = air flow rate (m^3 h^{-1})

A = chamber bottom area (m^2)

Temperature correction for ammonia emission rates

To be consistent with the data-processing interval for ammonia emission rates, the temperature data was segmented into 2-h intervals for each day. The chamber headspace temperature for each 2-h period (5-min interval) was averaged. The chamber headspace temperature on different days was also different, so the average chamber headspace temperature for each 2-h period during three weeks was calculated and used to correct for ammonia emission rates.

The ammonia emission rate correction for temperature was based on the Van't Hoff Equation, which can correct Henry's constant (K_H) for temperature (Atkins and De Paula, 2006):

$$\frac{K_{H2}}{K_{H1}} = e^{[\frac{-\Delta H}{R} \times (\frac{1}{T_2} - \frac{1}{T_1})]} \tag{2-2}$$

where

K_{H2} = Henry's constant at T_2 (dimensionless, $=[NH_3]_{(aqueous)}/[NH_3]_{(gaseous)}$)

T_2 = average temperature for the 2-h period in all measurement days, K

K_{H1} = Henry's constant at T_1

T_1 = original temperature, K

ΔH = enthalpy of solution for ammonia, -7.29 kcal mol^{-1} (CRC and Knovel, 2008)

R = ideal gas constant, 0.001987 kcal K^{-1} mol^{-1}

Assume the ammonia concentration in liquid manure $[NH_3]_{(aqueous)}$ is constant. According to Henry's Law, correcting the NH_3 emission rate (g cow^{-1} d^{-1}) and gaseous NH_3 concentration (mg m^{-3}) from the original temperature (T_1) to average temperature (T_2) can be achieved by:

$$\frac{(NH_3\ \text{emission rate})_2}{(NH_3\ \text{emission rate})_1} = \frac{[NH_{3(g)}]_2}{[NH_{3(g)}]_1} = \frac{K_{H1}}{K_{H2}} = e^{[7.29/0.001987\times(\frac{1}{T_1}-\frac{1}{T_2})]} \tag{2-3}$$

In the study for Objective 2, the ammonia emission rate at each 2-h period was corrected to 15 ℃, also using Equation 2-3. This can benefit the comparison of ammonia emission rates through the year.

2.4.4.2 Statistical analysis

Two-tailed paired t-test in MS Excel was used to compare corrected ammonia emission rates between the treatments. The following comparisons were made: normal vs. low N, scraped vs. flushed, NS vs. LS, and NF vs. LF. The emission rate from two treatments was paired for each 2-h period. For instance, in the NS vs. LS test, the emission rate for NS and that for LS in 9:25 am - 11:25 am formed a pair, and those at 11:25 am - 1:25 pm formed the next pair. The normal vs. low N test included pairs for NS vs. LS plus pairs for NF vs. LF. The scraped vs. flushed test included pairs for NS vs. NF plus pairs for LS vs. LF. The temperature correction was to correct ammonia emission rates using the average temperature of different weeks for each 2-h period, but the paired t-test was to remove the effects of temperature variations in different time of day on ammonia emission rates and focus on the effects of treatments.

The null hypothesis for each comparison was that the mean of the differences of each paired observations during a 2-h period was zero. The alternative hypothesis for each comparison was that the mean of the differences of each pair was not zero, i.e.:

$$\mathrm{H_0}: \mathrm{Mean}\ (\mathrm{A_i} - \mathrm{B_i}) = 0$$

$$\mathrm{H_a}: \mathrm{Mean}\ (\mathrm{A_i} - \mathrm{B_i}) \neq 0$$

where

A_i, B_i – ammonia emission rates from two treatments

i – the i^{th} 2-h period since the beginning of measurement during a measurement day

The p-value was set at 0.05. If the calculated p-value was less than 0.05, the null hypothesis was rejected, which suggested that ammonia emission rates for two treatments were significantly different; otherwise, the null hypothesis was accepted, which suggested that ammonia emission rates for two treatments were not significantly different.

All comparisons for manure characteristics between two treatments were conducted by two-tailed non-paired t-test with equal variance in MS Excel. A calculated p-value less than 0.05 suggested that the difference was significant; otherwise, it was not significant.

2.5 Results and Discussions

2.5.1 Objective 1: Effects of diets and manure removal practices on ammonia emission rates

The data of the first week of measurement from 08/12/2007 to 08/18/2007 (two weeks after diet application and one week after tank seeding) was excluded, because a settling period was expected for the manure in storage tanks. Manure TS and pH can affect ammonia emissions (Gilbertson *et al.*, 1981; Muck and Steenhuis, 1982), but in this study, manure TS and pH in the first week were significantly different from those in following 3 weeks, based on non-paired t-tests. The manure TS and pH in the four weeks are shown in Figure 2-3. The TS for scraped manure tanks was 7.3±0.5% and 5.5±0.7% in the first week and in following three weeks, respectively (P<0.05). The TS for flushed manure tanks was 1.3±0.7% and 2.7±0.7% in the first week and in following three weeks, respectively (P<0.05). The pH for scraped manure tanks was 6.0±0.3 and 6.5±0.1 in the first week and in following three weeks, respectively (P<0.05). The pH for flushed manure tanks was 7.3±0.2 and 6.4±0.3 in the first week and in following three weeks, respectively (P<0.05). As reported in literature, 2% TS in stored beef cattle manure caused significantly higher ammonia emission rates than 12% TS (Gilbertson *et al.*, 1981), and pH less than 7 can make NH_4^+ more favorable than NH_3 and thus reduce ammonia emissions from animal manure storage (Hartung and Phillips, 1994).

Therefore, it was assumed that the manure was still in a settling period in the first week of measurement. The data for the following three weeks (from 08/19/2007 to 09/08/2007) were used for manure characteristics and ammonia emission rates in the study for Objective 1.

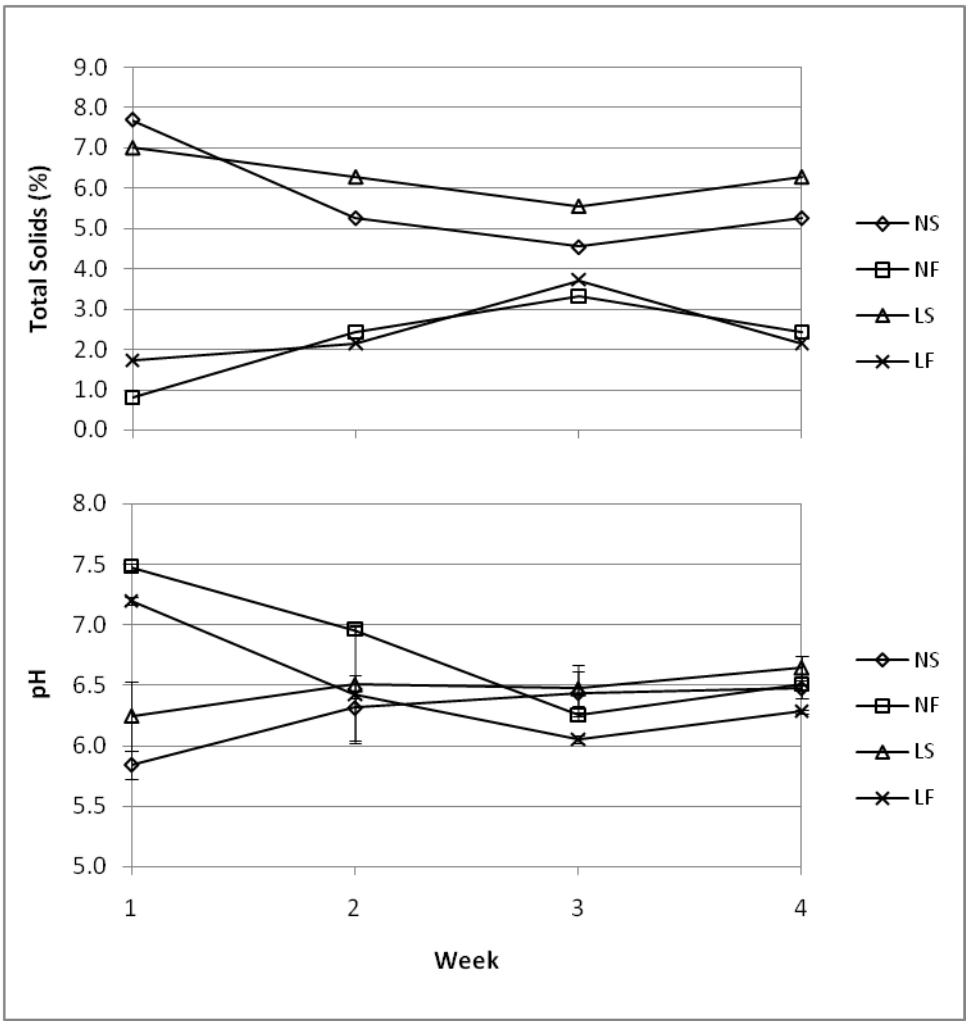

Figure 2-3. Total solids and pH of stored manure (from 08/12/2007 to 09/08/2007)

(NS - scraped manure for normal diet, NF - flushed manure for normal diet, LS - scraped manure for low N diet, LF - flushed manure for low N diet)

2.5.1.1 Manure characteristics

The manure characteristics for four storage tanks from 08/19/2007 to 09/08/2007 are listed in Table 2-2. The TKN concentrations for NS, NF, LS, and LF were 1922 ±719, 881 ±137, 1835 ±487, and 701 ± 65 mg N L^{-1}, respectively. The TAN concentrations for NS, NF, LS, and LF were 664 ±

359, 165 ± 24, 548 ± 180, and 187 ± 21 mg N L^{-1}, respectively. The manure pH for NS, NF, LS, and LF were 6.3 ± 0.1, 6.4 ± 0.3, 6.4 ± 0.1, and 6.1 ± 0.1, respectively. Manure TKN, TAN, TS and TP for the flushed manure were lower (P<0.05, based on non-paired t-tests) than those for the scraped manure, because the flushed manure was more diluted. However, none of the manure characteristics for the low N diet was significantly different from the normal diet. This was because that the dietary N reduction mainly reduced the urine N, but a considerable portion of the urine was in floor ditches and hard to collect. The different dietary N and manure removal practices didn't affect the N : P ratio, which was similar to the requirement for typical crops, approximately 4.5~5:1 (VanHorn *et al.*, 1996).

Table 2-2. Mean characteristics of stored manure (from 08/19/2007 to 09/08/2007)

	Number of samples for each tank	**NS †**	**NF**	**LS**	**LF**
Manure weight (kg)	3	145 ± 43 ‡	180 ± 58	146 ± 47	173 ± 58
TKN (mg N L^{-1})	3	1922 ± 719	881 ± 137	1835 ± 487	701 ± 65
TAN (mg N L^{-1})	3	664 ± 359	165 ± 24	548 ± 180	187 ± 21
pH	9	6.3 ± 0.1	6.4 ± 0.3	6.4 ± 0.1	6.1 ± 0.1
TS (%)	3	5.0 ± 4.1	2.7 ± 0.5	6.0 ± 4.3	2.7 ± 0.9
COD (g L^{-1})	3	42.5 ± 0.4	13.9 ± 7.0	69.4 ± 44.5	19.9 ± 1.2
TP (mg L^{-1})	3	423 ± 42	161 ± 27	422 ± 15	187 ± 12
N : P	2	3.6 ± 0.1	5.1 ± 0.1	3.7 ± 0.5	3.6 ± 0.1

† NS - scraped manure for normal diet, NF - flushed manure for normal diet, LS - scraped manure for low N diet, LF - flushed manure for low N diet.

‡ Mean ± standard deviation.

2.5.1.2 Ammonia emission rates

From 08/19/2007 to 09/08/2007, ammonia emission rates (after temperature correction) from scraped manure tanks were in a similar trend with the diurnal changes of chamber headspace temperature, but emission rates from flushed manure were too low to show this trend clearly (Figure 2-4). The peak of emissions occurred during 1 pm - 4 pm. The error bars show variances during different weeks.

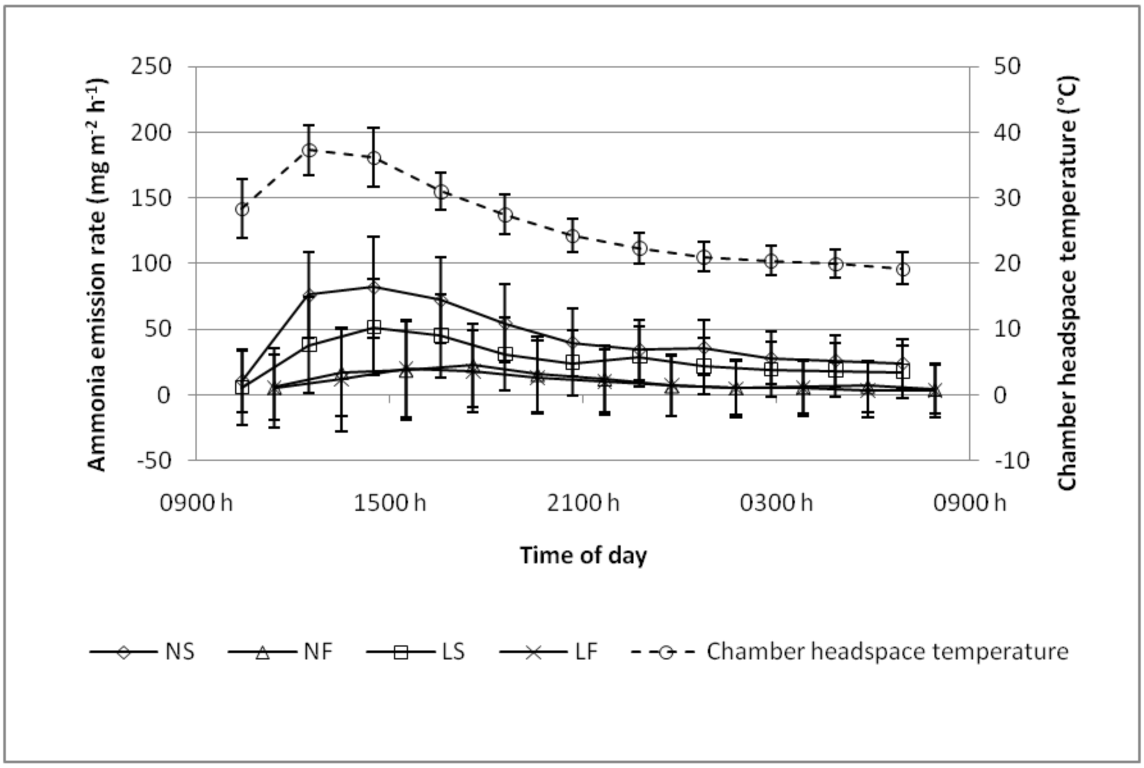

Figure 2-4. Chamber headspace temperature and ammonia emission rate vs. time (from 08/19/2007 to 09/08/2007)

(NS - scraped manure for normal diet, NF - flushed manure for normal diet, LS - scraped manure for low N diet, LF - flushed manure for low N diet)

Table 2-3 shows the chamber headspace temperature, manure surface temperature and ammonia emission rates (after corrected for temperature) for four tanks from 08/19/2007 to 09/08/2007. The chamber headspace temperature for NS, NF, LS and LF were 26.0 ± 6.9, 25.8 ± 6.8, 26.6 ± 6.5, and 27.2 ± 6.7 ℃, respectively. The manure surface temperature for NS, NF, LS and LF were 23.5 ± 3.0, 22.8 ±3.3, 24.2 ±3.4, and 23.1 ±3.3 ℃, respectively. Ammonia emission rates for NS, NF, LS and LF were 43.9 ± 48.0, 10.9 ± 8.7, 27.4 ± 27.3, and 9.3 ± 7.8 mg m^{-2} h^{-1}, respectively. Ammonia emission rates from tanks for the normal diet and the low N diet were 27.4 ±38.1 and 18.4 ±21.9 mg m^{-2} h^{-1}, respectively. Ammonia emission rates from tanks with scraped and flushed manure were 35.6 ±39.6 and 10.1 ±8.2 mg m^{-2} h^{-1}, respectively. The chamber headspace temperature for all tanks was at a similar level; it is also true for manure surface temperature. However, the mean chamber headspace temperature for different tanks was not exactly equivalent because: (1) not all tanks were measured in same days; (2) even in the same day, the chamber greenhouse effect caused temperature differences in the headspaces of two chambers. The separation and greenhouse effect of the chamber also made the chamber headspace temperature higher than the air temperature in hot weather conditions.

Table 2-3. Mean temperature and ammonia emission rates (from 08/19/2007 to 09/08/2007)

	Number of samples for each tank	Diet	Scraped	Flushed
Chamber headspace temperature (℃)	33	normal	26.0 ±6.9	25.8 ±6.8
		low N	26.6 ±6.5	27.2 ±6.7
Manure surface temperature (℃)	33	normal	23.5 ±3.0	22.8 ±3.3
		low N	24.2 ±3.4	23.1 ±3.3
Ammonia emission rate (mg m^{-2} h^{-1})	33	normal	43.9 ±48.0	10.9 ±8.7
		low N	27.4 ±27.3	9.3 ±7.8

Based on results of paired t-tests (Table 2-4), ammonia emission rates from the two tanks with the low N diet were significantly lower (P<0.0001; 33% lower by average) than those from the two tanks with the normal diet; ammonia emission rates from the two flushed tanks were significantly lower (P<0.0001; 72% lower by average) than those from the two scraped tanks. In addition, ammonia emission rates from scraped manure for the low N diet was significantly lower than for the normal diet (P<0.0003; 38% lower by average), and ammonia emission rates from flushed manure for the low N diet was significantly lower than for the normal diet (P<0.02; 14% lower by average). In conclusion, both dietary N reduction and manure flushing are recommended to reduce ammonia emission rates from dairy manure storage tanks (during summer operation).

Table 2-4. Paired t-tests results for ammonia emission rates (from 08/19/2007 to 09/08/2007)

Tests †	**Number of samples for each group**	**P-value**
normal vs. low N	66	<0.0001
scraped vs. flushed	66	<0.0001
NS vs. LS ‡	33	0.0003
NF vs. LF	33	0.02

† Paired for each 2-h period (e.g., 9:25-11:25 am).

‡ NS - scraped manure for normal diet, NF - flushed manure for normal diet, LS - scraped manure for low N diet, LF - flushed manure for low N diet.

It is difficult to compare ammonia emission rates from manure storage among different studies, because parameters such as the initial manure N content, manure retention time on barn floor, dilution ratio for flushing, and the ratio of storage volume to surface area can vary largely. Ammonia emission rates in this study were lower than some other studies (Table 2-5) due to two reasons. First, the manure pH was lower than in other studies. Second, the manure N content (especially urine N) was lower, since a considerable portion of the urine was in floor ditches and hard to collect. Urea N in urine is known as an important source of ammonia emissions (Muck, 1982). Both the lower pH and manure N content were also due to the water addition in the first day and the rainstorm dilution later on. In comparison, manure storage facilities in most other studies were not placed in open environment or accepting water addition.

Table 2-5. Comparison of ammonia emissions from dairy manure storage with comparable studies

	Present study †	**(Külling *et al.*, 2001)**	**(Amon *et al.*, 2006)**	**(Sparks, 2008)**	**(Dinuccio *et al.*, 2008)**	**(Rumburg *et al.*, 2008)**
Storage facility size	Pilot-scale (1.1 m^3, 2.0 m^2)	Lab-scale (10L, 0.05 m^2)	Pilot-scale (10 m^3, 4 m^2)	Lab-scale (~133 L)	Lab-scale (1.5 L)	On-farm storage lagoon
Storage period, d	28	49	80	0.5-4	30	>350
Manure N (mg L^{-1})	TKN=1922, 881, 1835, and 701; TAN=664, 165, 548, and 187 (for NS, NF, LS and LF)	TKN=6010, 4630, and 3330; Urine N=2960, 1610, and 780 (for dietary N=175, 150, and 125 g kg^{-1})	TKN=3250~3960	TKN=3998~7603; TAN/TKN=50% (for scraped); TKN=861~1463; TAN/TKN=5% (for flushed)	TKN=3580; TAN=1470	TAN=530~660
Temperature, ℃	23±3	20	10	5-25	5; 25	11; 27
Manure pH	6.3±0.2	Initial: 7.0-8.3; After 49 d: 6.3-7.0	7.1-7.9	Initial: 6.9-7.1; After 24 h: 8.6	7.1	7.8
Ammonia measurement method	Dynamic chamber and photoacoustic gas analyzer.	Dynamic chamber and chemi-luminescent analyzer.	Dynamic chamber (covering 27 m^2) and FTIR detection.	Dynamic chamber and photoacoustic gas analyzer.	Dynamic chamber and photoacoustic gas analyzer.	Downwind measuring with differential optical absorption spectroscopy.
Ammonia emission rate, mg m^{-2} h^{-1}	44, 11, 27, 9 (for NS, NF, LS, LF)	486, 256, 151 (for dietary N=175, 150, 125 g kg^{-1})	53	~360 and ~90 (for scraped and flushed manure)	~25 and ~100-150 (at 5 and 25 ℃)	110 and 540 (at 11 and 27 ℃)

† From 08/19/2007 to 09/08/2007. NS - scraped manure for normal diet, NF - flushed manure for normal diet, LS - scraped manure for low N diet, LF - flushed manure for low N diet.

2.5.2 Objective 2: Seasonal effects on ammonia emission rates

2.5.2.1 Manure characteristics

Figure 2-5 shows the weight of manure in both tanks through one year. The sharp increasing on 10/26/2007 was due to a heavy rainstorm (12.6 cm). The sharp decreasing of flushed manure on 01/07/2008 and the decreasing of both manure on 04/20/2008 were because that 2/3 of the manure was removed when the tanks filled up.

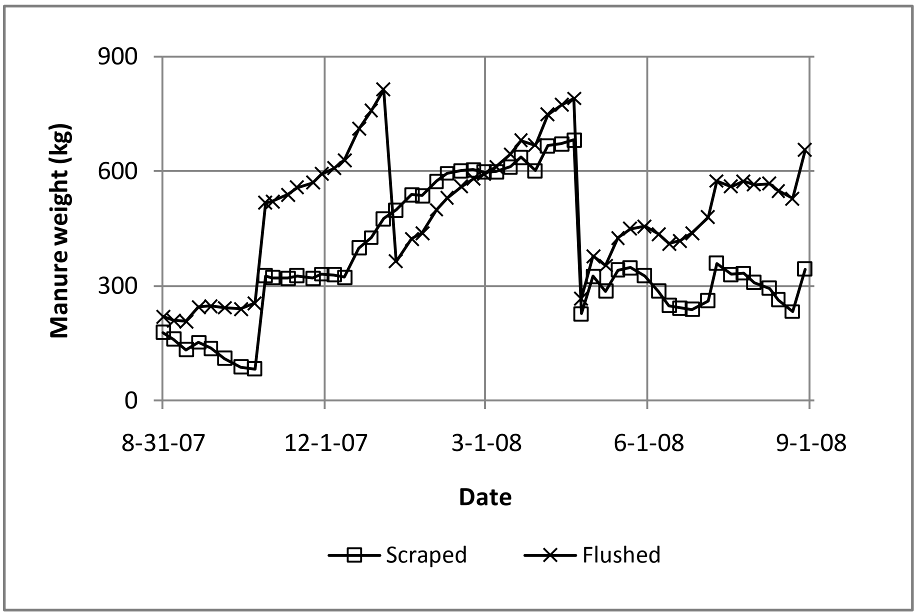

Figure 2-5. Manure weight vs. time

Manure characteristics from 09/01/2007 to 08/31/2008 are listed in Table 2-6. Most manure characteristics were concentrations, and thus dependent on manure volume or weight. Since all tanks were located in open air, the change of manure weight was affected by the precipitation. In winter 2007/2008 and spring 2008, manure concentrations of TKN, TAN, TS, COD and TP were mostly lower than in the earlier study for Objective 1 (for both scraped and flushed tanks). This was due to the dilution of rainstorms, especially the rainstorm from 10/24/2007 to 10/26/2007. In summer 2008, most of those concentrations mentioned above increased again, which may be due to the higher evaporation of water under higher air temperature. From spring to summer 2008, the manure TKN increased by 46% and 52% for scraped and flushed manure, respectively. However, the manure TAN increased by 88% and 117% for scraped and flushed manure, respectively. The percentages of TAN increasing from spring to summer were higher than those of TKN, because the biological degradation rate of organic N to inorganic N increases with temperature. The N : P ratio of both scraped and flushed manure in the year (3.0~5.3:1) was similar to the requirement for typical crops, approximately 4.5~5:1 (VanHorn *et al.*, 1996).

Table 2-6. Mean characteristics of stored manure (from 09/01/2007 to 08/31/2008)

		Fall 2007		**Winter 2007/2008**		**Spring 2008**		**Summer 2008**	
	Number of samples for each tank in each season	Scraped †	Flushed	Scraped	Flushed	Scraped	Flushed	Scraped	Flushed
Manure weight (kg)	13	216 ± 107 ‡	380 ± 165	500 ± 102	577 ± 131	486 ± 175	557 ± 176	288 ± 44	519 ± 76
TKN (mg N L^{-1})	13	1808 ± 1617	700 ± 281	853 ± 165	543 ± 103	914 ± 145	615 ± 97	1332 ± 266	934 ± 735
TAN (mg N L^{-1})	13	384 ± 212	216 ± 88	269 ± 64	206 ± 42	146 ± 48	86 ± 17	274 ± 59	187 ± 47
pH	13	7.2 ± 0.6	6.8 ± 0.4	6.7 ± 0.2	6.7 ± 0.4	6.5 ± 0.3	6.4 ± 0.3	7.0 ± 0.3	6.8 ± 0.4
TS (%)	13	4.4 ± 1.8	2.8 ± 0.8	2.7 ± 0.7	2.0 ± 0.2	3.0 ± 0.9	2.1 ± 0.7	4.2 ± 1.2	1.7 ± 0.5
COD (g L^{-1})	13	43.2 ± 17.5	13.2 ± 4.8	18.6 ± 7.4	11.7 ± 2.1	23.4 ± 6.0	18.5 ± 3.9	23.0 ± 15.5	13.4 ± 4.1
TP (mg L^{-1})	13	362 ± 73	187 ± 53	256 ± 85	120 ± 7	265 ± 35	136 ± 19	425 ± 97	184 ± 35
N : P	13	5.3 ± 3.0	4.1 ± 0.7	3.5 ± 0.3	4.5 ± 0.5	3.4 ± 0.3	4.3 ± 0.2	3.0 ± 0.3	4.3 ± 0.6

† Normal diet only.

‡ Mean ± standard deviation.

The pH of scraped manure was 7.2 ±0.6, 6.7 ±0.2, 6.5 ±0.3 and 7.0 ±0.3 for fall, winter, spring and summer, respectively. The pH of flushed manure was 6.8 ±0.4, 6.7 ±0.4, 6.4 ±0.3 and 6.8 ±0.4 for fall, winter, spring and summer, respectively. Manure pH in fall and summer was higher than in winter and spring for both tanks. In a previous study by Ro *et al.* (2008), the pH in untreated manure storage in fall and summer were also slightly lower than in winter and spring, but the reason was not suggested. Figure 2-6 shows the pH of manure in both tanks through the year. The pH of scraped manure in the first several weeks increased from 6.5 to 8.3, but since the rainstorm from 10/24/2007 to 10/26/2007, the pH dropped to approximately 7.2.

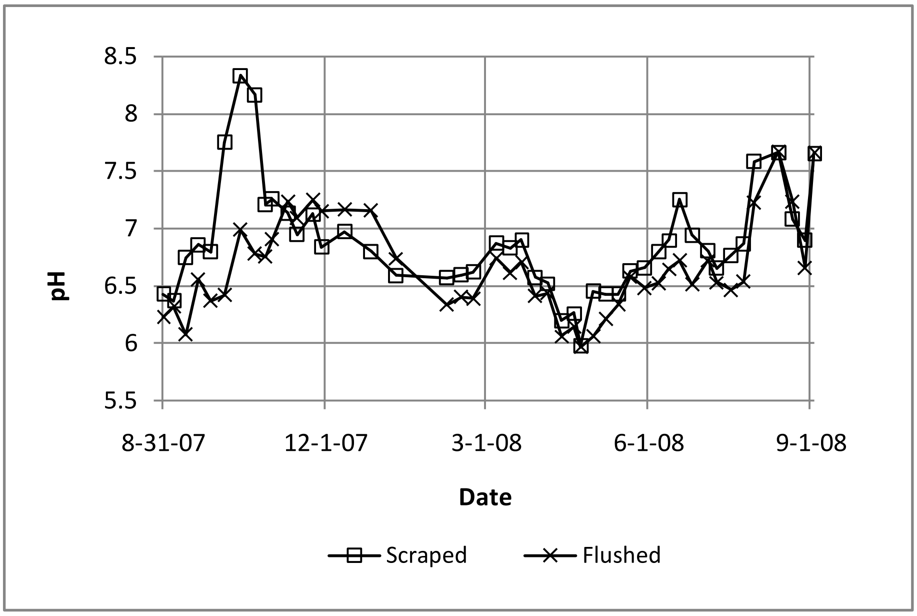

Figure 2-6. Manure pH vs. time

2.5.2.2 Ammonia emission rates

Figure 2-7 shows the chamber headspace temperature and ammonia emissions rates with time of day in different seasons. The “meteorological seasons” (divided by Mar 1, Jun 1, Sep 1, and Dec 1) rather than “astronomical seasons” were used in this study. During the whole year when two tanks (NS and NF) were studied, ammonia emission rates tracked well with the diurnal air temperature trends, as well as the seasonal temperature trends. The second peak of emission rates at late night (1-3am) for each tank during fall season remains unexplained.

Ammonia emission rates from scraped manure for fall, winter, spring, and summer were 7.4 ± 8.6, -0.5 ± 1.2, 1.1 ± 1.9, and 5.8 ± 2.7 mg m^{-2} h^{-1}, respectively. Ammonia emission rates from flushed manure for fall, winter, spring, and summer were 3.9 ± 4.2, -0.5 ± 0.9, 0.8 ± 1.4, and 4.4 ± 1.2 mg m^{-2} h^{-1}, respectively.

During winter and spring there were negative emission rates reported (after correction with background ammonia concentration). The background ammonia in this case was likely from an open dairy feedlot approximately 5 m away from the experimental tanks. The chamber ammonia concentrations were measured for whole day. During the cold times in the day when air temperature dropped to near or below 0 ℃, the ammonia concentration dropped to 1-2 mg m^{-3}. However, the background ammonia concentration (2.7 ± 0.3 mg m^{-3}) was only measured at morning times (before and after tank measurement), when it was typically not too cold. Further, those extremely low concentrations at cold times were not very reliable, most likely because: (1) the air temperature was below the recommended operation temperature (5-40 ℃) of the monitor; (2) the ammonia concentration was not far from the detection limit of the monitor (~0.4 mg m^{-3}). Therefore, it is most possible that these negative emission rates were actually near zero.

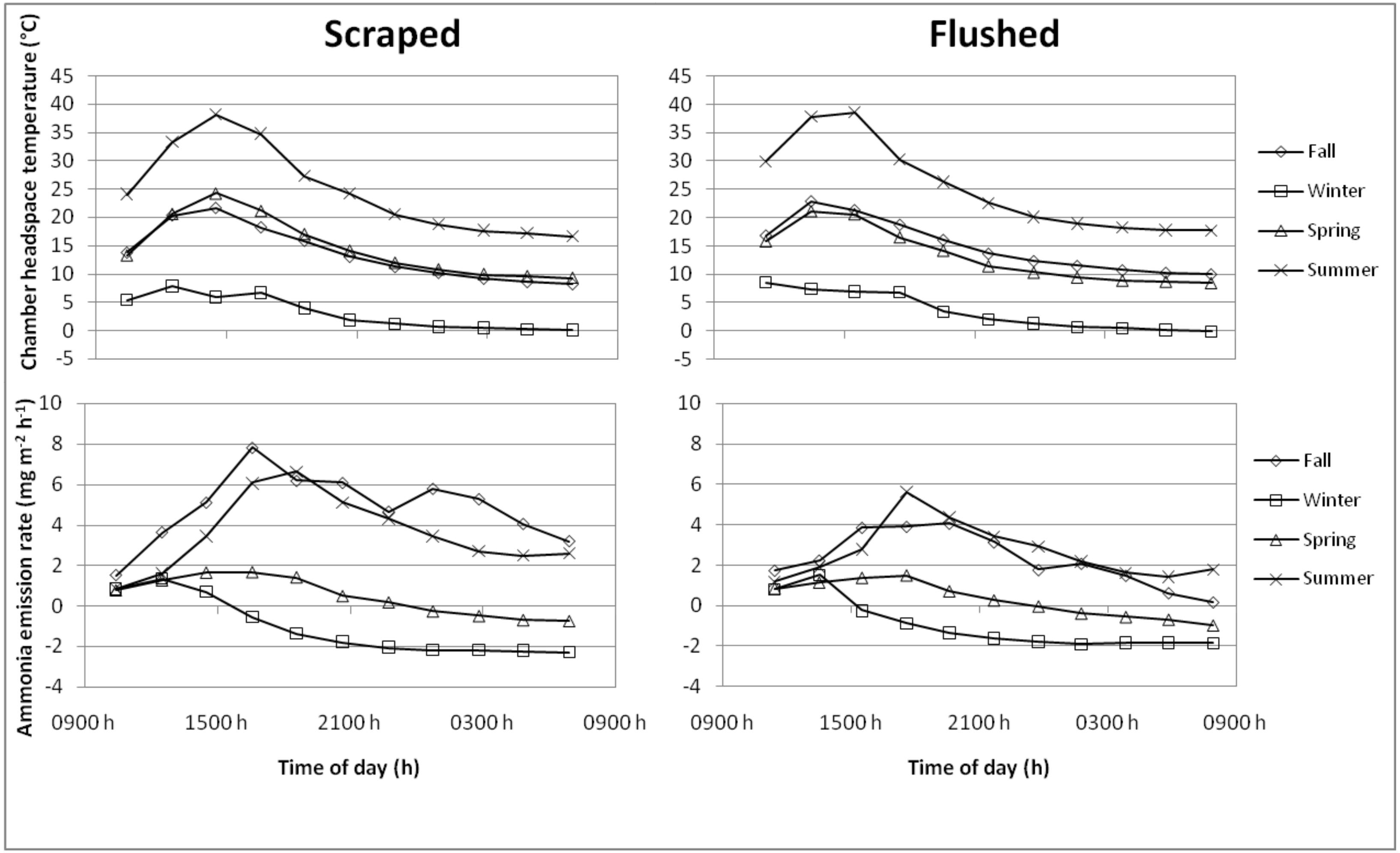

Figure 2-7. Average ammonia emission rate and temperature vs. time of day in different seasons

Ammonia emission rates were mainly affected by air temperature, but also affected by manure pH. High manure pH can enhance ammonia dissociation and emissions due to the acid-basic equilibrium (Ni, 1999; Sparks, 2008). Ammonia emission rates in winter and spring were lower than in fall and summer (Figure 2-6 and Figure 2-8), because both the temperature and pH were lower in winter and spring. During winter, emissions were reduced also due to snow and ice, which covered the manure surface (the chambers were placed on tanks only during measurement days). The increasing of ammonia emission rates from both tanks in summer 2008 were also caused by the increasing of TAN concentration, as discussed in Section 2.5.2.1. Mass balance for N can be useful to determine whether the ammonia N loss matches the change of manure N quantity, but it was not successfully conducted in this study due to the variance in the manure N analysis.

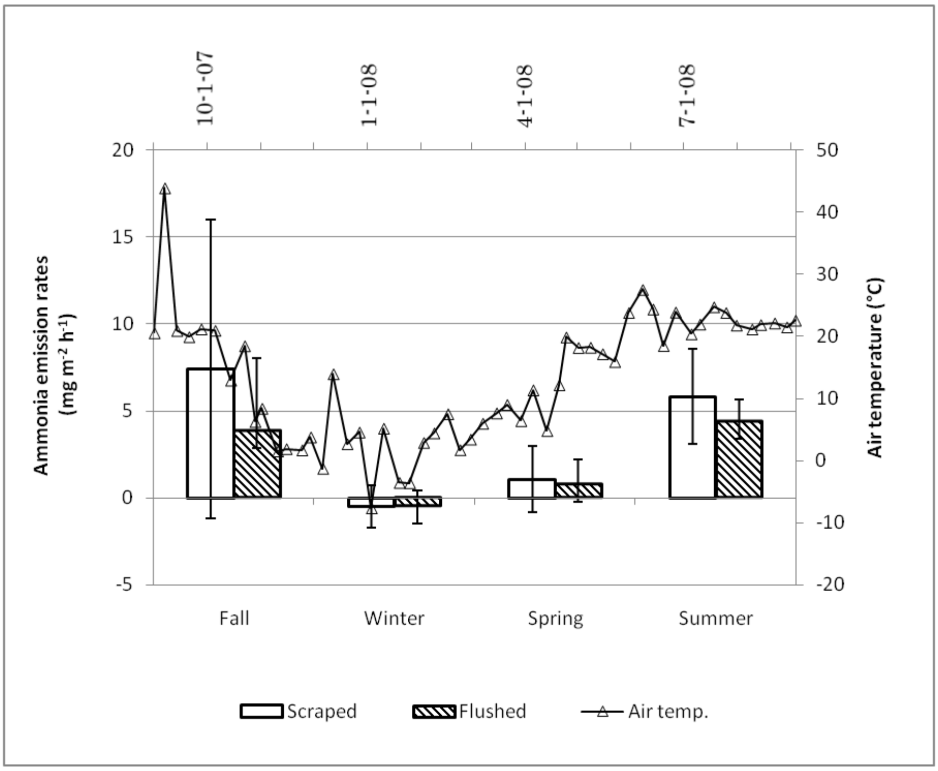

Figure 2-8. Air temperature and ammonia emission rate vs. date

The heavy rainstorm from 10/24/2007 to 10/26/2007 (12.6 cm) reduced the TAN for both tanks, and reduced the pH for scraped manure tank. As a result, ammonia emission rates from both tanks were significantly reduced for both tanks, compared to the former weeks. Rainstorms can also explain why the seasonal averages of emission rates from the scraped manure tank in fall 2007 and summer 2008 (Figure 2-8) were lower than in the study for Objective 1 during late summer to early fall 2007 (Figure 2-4). This effect of rainstorm is consistent with some previous studies, which reported that rainfall events can reduce N concentration in liquid manure (Westerman *et al.*, 2006) and ammonia emissions (Sommer and Olesen, 2000). The rainstorm in this study also reduced the difference of ammonia emission rates from scraped manure and flushed manure because both tanks were highly diluted (Figure 2-7).

Differences of temperature at the manure surface and at different depths may cause vertically inconsistent ammonia concentrations, since temperature affects ammonium dissociation and ammonia diffusion processes. Figure 2-9 shows the vertical manure temperature data during spring and summer 2008. For each hour, the mean temperature in 19 weeks was used. Error bars show variances at different time of day (N=24). The temperature at manure surface and bottom was lower than that in middle (0.15-0.25 m from surface). In natural water bodies such as lakes, it is also common that during spring and summer there is a temperature stratification phenomenon after spring turnover, when the lower layer (below the thermocline line, at least 10m from surface) has a lower temperature than the top layer (Antonopoulos and Gianniou, 2003; Mccormick and Scavia, 1981). However, since the manure depth in this study was shallow, these two phenomena may not be comparable. In this study, the temperature at manure surface was close to air temperature due to fast heat transfer at the interface, but the manure temperature at middle depth was higher than the surface temperature, possibly due to some heat production by biological activities in the liquid. The ammonia production and dissociation rate at the middle depth should be highest in the vertical direction during spring and summer. Using manure surface temperature to determine ammonia emissions from stored manure, especially in modeling work, is not accurate.

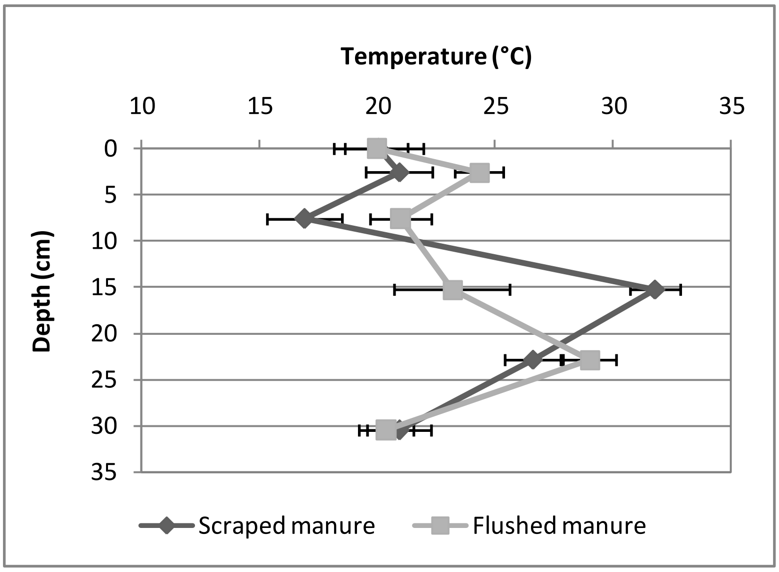

Figure 2-9. Manure temperature vs. depth during spring to summer 2008

The seasonal trend of ammonia emissions from manure storage in this study is consistent with previous studies that reported lower ammonia emissions in colder seasons than in warmer seasons (Ni, 1999; Rumburg *et al.*, 2008). Westerman *et al.* (2006) reported that the trend of N content in swine manure storage is inverse to the seasonal temperature trend, and they suggested that this was due to higher ammonia emissions in warmer seasons. Ammonia emissions increase with temperature not only because of the increased volatilization, but also because of the increased N mineralization (Muck and Steenhuis, 1982; Whitehead and Raistrick, 1993).

2.6 Conclusions

In this study, ammonia emission rates from four dairy manure storage tanks with four treatments - scraped manure for the normal diet (NS), flushed manure for the normal diet (NF), scraped manure for the low N diet (LS), and flushed manure for the low N diet (LF) - were compared for three weeks. The first two tanks were also studied for one year to determine seasonal effects on ammonia emission rates.

As the dietary N content is reduced (from 17.8% to 15.9% crude protein), the manure N content was not significantly affected, but ammonia emission rates from manure storage tanks were reduced by 33%. Further, flushing manure decreases emission rates by 72% compared to scraping manure. In another word, both dietary N reduction and manure flushing are recommended to reduce ammonia emission rates from dairy manure storage tanks.

Ammonia emission rates were higher in summer and fall, due to higher air temperature and higher manure pH. Manure concentrations of TKN and TAN mostly increased in summer due to the higher evaporation of water under higher air temperature. The percentages of TAN increasing from spring to summer were higher than those of TKN, because the biological degradation rate of organic N to inorganic N increases with temperature. A heavy rainstorm in fall 2007 diluted the manure and reduced ammonia emission rates. During winter, emissions were reduced due to lower temperatures and snow and ice, which covered the manure surface. More attention should be paid to reduce ammonia emissions in warmer seasons, e.g., by covering the storage facilities.

Suggestions to farmers are given: (1) In a view of the whole dairy operation system, manure flushing is better than scraping in terms of reducing ammonia emissions (both from barn floors and from manure storage). (2) Dietary N reduction is useful to reduce ammonia emissions from manure storage for both scraped and flushed manure. Dietary N reduction is the only way of reducing total ammonia loss in the whole system, rather than just transferring ammonia emissions from one period to another or from one facility to another. However, considering the milk quality, a diet with lower than 15.9% CP (or 8.8% RDP) is not suggested.

Future works may consider: (1) using measurement methods which are non-intrusive to natural air flow (such as meteorological method), instead of flux chamber system; and (2) using the data from this study to improve process-based emission models to better predict ammonia emission rates from manure storage tanks.

2.7 Acknowledgements

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Chapter 3. Future Work: Modeling Ammonia Emissions from Dairy Manure Storage Tanks

3.1 Introduction

Building mathematical and computer models is more cost-effective and time-effective than experiments to determine and predict ammonia emission rates from livestock operations based on process description and calibration with experimental data. The sensitivity analysis on the model parameters can also help to identify the important affecting factors. Two different strategies are usually used for ammonia emission models: empirical models and process-based models. Empirical models are built based on experimental data or other observations, usually using regression equations. They are easily developed and can be used quickly in similar conditions, but less reliable and not applicable well to different conditions because the parameters could vary considerably in different situations, especially for manure storage. Process-based models are built based on the real processes (e.g., chemical and biological reactions, mass transfer mechanisms), which could be more complex and usually more reliable, as long as the processes and parameters are properly described. Even in process-based models, it is sometimes inevitable to use some coefficients which are empirical.

Numerous modeling studies have been conducted on ammonia emissions from dairy farms and other animal operations (Elzing and Monteny, 1997; Liang *et al.*, 2002; Monteny *et al.*, 1998; Ro *et al.*, 2008; Zhang *et al.*, 1994). However, the accuracy and reliability of the existing models are usually evaluated by independent evaluation standards, so large uncertainties exist among the different models and between model and experimental data (Zhang *et al.*, 2008), which brings a challenge and need to conduct more comprehensive modeling work.

Ammonia is emitted from dairy manure through four processes: ammonia production, dissociation, diffusion, and volatilization. Temperature has effects to all these processes, so it is necessary to more deeply determine the extents of those effects in manure storage. The existing models mostly used one constant temperature and one constant NH_3 concentration for the whole liquid manure. However, based on TAN and pH value for the whole liquid manure and detailed vertical temperature gradients (calculated by heat transfer equations), the detailed NH_3 conversion conditions at different depths and a more accurate emission rates from the surface can be calculated.

Muck and Steenhuis (1982) considered the vertical ammonia diffusion from bottom to surface as a previous step before the volatilization on surface. Zhang *et al.* (1994) reported lower pH and higher NH_3-N in lower layers than in higher layers. However, no study was seen to include the vertical temperature gradient in model. Two of the great research needs in modeling ammonia emission from manure storage as suggested were the consideration of vertical temperature gradient (Liang *et al.*, 2002) and prediction of manure pH (Sommer *et al.*, 2006).

The objective of this future work is to build a process-based model for ammonia emissions from liquid manure storage tanks incorporating vertical temperature gradients and seasonal pH changes.

3.2 Model descriptions

This model could include: (1) sub-model for manure volume (considering daily manure inflow, water evaporation, and precipitation); (2) sub-model for air temperature as function of date and time; (3) sub-model for manure temperature at different depths as function of date, time and depth; (4) sub-model for average manure pH as function of date; and (5) incorporating the manure temperature gradients into the four processes: ammonia production, dissociation and diffusion at different depths, and volatilization at the surface.

This model could be calibrated using half of our experimental data obtained from a year-long study in Virginia, and validated using the other data as well as data from other literature. Eventually, the ammonia emission rate as function of time in a year and the whole-year ammonia emissions could be produced, and the sensitivity of emissions on different factors could be determined.

The governing equation of the model is still the same as in most previous models as reviewed by Ni (1999):

$$q = K_m\left([NH_3]_{g,0} - [NH_3]_{g,\infty}\right) \tag{3-1}$$

where

q = ammonia emission rate (mg m^{-2} s^{-1})

K_m = convective mass transfer coefficient (m s^{-1})

$[NH_3]_{g,0}$ = concentration of gaseous NH_3 at the manure surface (mg m^{-3})

$[NH_3]_{g,\infty}$ = concentration of gaseous NH_3 in the free air stream (mg m^{-3})

The convective mass transfer coefficient K_m ranges from 11.7×10^{-3} to 1.3×10^{-6} m s^{-1}, as a function of air velocity and air or manure temperature (Ni, 1999).

3.2.1 Assumption for constant TKN

In manure storage tanks, even though the TKN quantity (g N) in the tanks is accumulated because of the daily addition of manure (e.g., every 6 h as floor flushing interval), the ammonia emission rate is only related to the TAN concentration at the surface layer. The daily manure addition increases the manure volume, but not the TKN concentration. The seasonal manure removal for land application reduces the manure volume, but not the N concentrations either, because the manure is usually mixed before and while pumping. Only extremely heavy rainstorms can significantly dilute the TKN concentration, but the frequency of those rainstorms is very low in climates similar to Blacksburg, Virginia (only once during one year in our study). Based on our observations, the daily ammonia-N emissions accounted for 3.4-7.6% of the daily manure-N added, or ~0.4-0.7% of TKN quantity in the whole tank, but the TKN concentration in the manure tank were not changing significantly at most time of the year. In this modeling study, the TKN concentration in manure tank is assumed to be constant all the time and can be applied to similar climates. In this way, only temperature and pH are the key factors to ammonia emissions.

3.2.2 Sub-model of manure volume and depth

Although the manure volume does not affect the TKN and TAN concentrations, it is still important in this study because the volume determines the depth of manure storage, while the depth could be important as the temperature gradient being studied. Assume that at day 1, 91, 181, and 271, manure volume (V) comes back to initial volume (V_0) because of seasonal removal for land application. The manure volume at a time t (day of year) can be estimated by:

$$V(t) = V_0 + (V_{in} + A \times Prec. - Evap.) \times Res.\left(\frac{t}{90}\right) \quad (3\text{-}2)$$

$$d = V(t)/A \quad (3\text{-}3)$$

where

$V(t)$ = manure volume at time t, m^3

V_0 = initial volume, m^3

V_{in} = manure inflow or addition rate, $m^3\ d^{-1}$

A = surface area of storage, m^2

Prec. = average precipitation, m d^{-1}

Evap. = average water evaporation rate, $m^3\ d^{-1}$

Res. (t/90) = residual of t/90, d

d = depth, m

The effect of ammonia emissions on volume change is neglected. Based on our experimental data of manure weight, manure addition, and precipitation, the major factors can be determined. The negligibility of water evaporation effect can be conducted by making regressions with the other parameters and examining the significance of error term (because the water evaporation effect has to be included in error term). The density of both scraped and flushed dairy manure was assumed to be 1 g L^{-1} (0.99±0.01 g L^{-1} in our experiments).

3.2.3 Sub-model for air temperature

The air temperature above manure storage tanks is changing diurnally and seasonally, which can be simulated by available mathematic models (e.g., sinusoid models, “humps” models). The most appropriate model for this study for a climate similar to Blacksburg, Virginia could be chosen, producing air temperature as function of date and time.

The year to year differences of air temperature and other weather conditions could be ignored in this model, if variances are small based on the weather data in Blacksburg, VA during the past 20 years or so.

3.2.4 Sub-model for manure temperature

Since the air temperature above manure storage tanks is changing diurnally and seasonally, the heat transfer between air and liquid manure and inside liquid manure is also changing periodically. Therefore, a manure temperature gradient at different depths exists, depending on air temperature, date, time and depth.

The significance of this sub-model was preliminarily estimated to determine whether it is necessary to look at the vertical temperature gradient. The estimation was focused on how much difference in ammonia dissociation can be caused by the observed temperature difference on vertical direction.

As observed from experimental studies, the difference between minimal and maximal temperature at different depths were considerable, ranging from 1.3-20.9 ℃. According to Equation 1.5 and 1.6, assuming constant TAN and pH=7 at all depths, the calculated maximal F (fraction of free ammonia, NH_3/TAN) was 1.1-4.4 times of the minimal F. This big difference in free ammonia in the liquid can considerably affect the diffusivity, which means that only using manure surface temperature or air temperature to calculate dissociation and diffusion is non-reliable. It could be worthy to investigate the vertical temperature gradients. The detailed differences in ammonia dissociation, diffusion and volatilization can only be known after solving the diffusion equations.

Finite element method can be used to solve the Partial Derivative Equations for heat transfer.

The output needed is the manure temperature gradient. The MatLab and COMSOL software can be used to solve the equations.

The major challenges of the manure-temperature model are: (1) the depth of the manure is changing with time; (2) the boundary condition (temperature on the manure surface) is also changing with time. Advanced computation methods need to be found to solve these problems, or the time range has to be divided to several sections (in each section the manure depth and the surface temperature are assumed to be constant).

In our experimental study, the tank was plastic so the wall and bottom was actually not very well insulated. The manure temperature at the middle depth was usually higher than surface and bottom. However, in real operations, both the ground basins and above-ground tanks are more thermally insulated at the wall and bottom (mostly concrete), so the manure temperature is changed mainly based on the heat transfer at manure surface. This model could be based on the assumption according to the real operations.

3.2.5 Sub-model for manure pH

Manure pH at different depths can be assumed to be consistent, but it changes with time. As observed in our experimental study, both the air temperature and manure pH were lower in winter and spring than in fall and summer. Slightly lower pH in untreated manure storage during winter and spring than during fall and summer was also found in a study by Ro *et al.* (2008). The prediction of pH needs improvement (Sommer *et al.*, 2006). In this future work, manure pH can be approximately modeled as a function of air temperature or time.

3.2.6 Computation for the rates of four processes at any depth

The manure TAN and pH for the whole liquid manure and the temperature at different depths estimated earlier can be used in computing the rates of the four processes: ammonia generation, dissociation, diffusion and volatilization. The first three processes occur at all the depths and thus depend on the temperature gradient, but ammonia volatilization occurs at the surface and thus only depends on manure surface temperature. Diffusion and volatilization are considered physical movements in vertical direction, but the other two are reactions without specific directions (Figure 3-1).

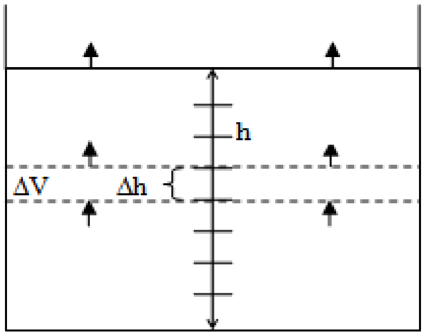

Figure 3-1. Vertical layers of manure storage

3.2.7 Model calibration and validation

The manure characteristics and environmental factors (air temperature and precipitation) can be used as input variables. Half of our year-long ammonia emission data obtained from two pilot-scale manure storage tanks (1100 L) in Blacksburg, Virginia can be used to calibrate the model parameters. The model accuracy standard by ASTM (2003) for air quality models can be used to calibrate and validate our model.

The other half of the year-long ammonia emission data can be used to validate the model. In addition, more data from several other studies reported in literature can be used to further validate the model (with necessary assumptions). The coefficient of determination (R^2) can be used during the validation process to evaluate the agreement between predicted and observed values. The same R^2 for two approaches (using surface temperature only and using vertical temperature gradient) can be compared to assess the significance of using vertical temperature gradient.

3.2.8 Sensitivity analysis

A global sensitivity analysis can be conducted to calculate the sensitivity of ammonia emissions on different affecting factors, and to identify the most influencing factors. The model can finally output the total NH_3 emissions in one year (g m^{-2} yr^{-1} or g cow^{-1} yr^{-1}).

Figure 3-2 shows the proposed flowchart of modeling ammonia emissions from manure storage.

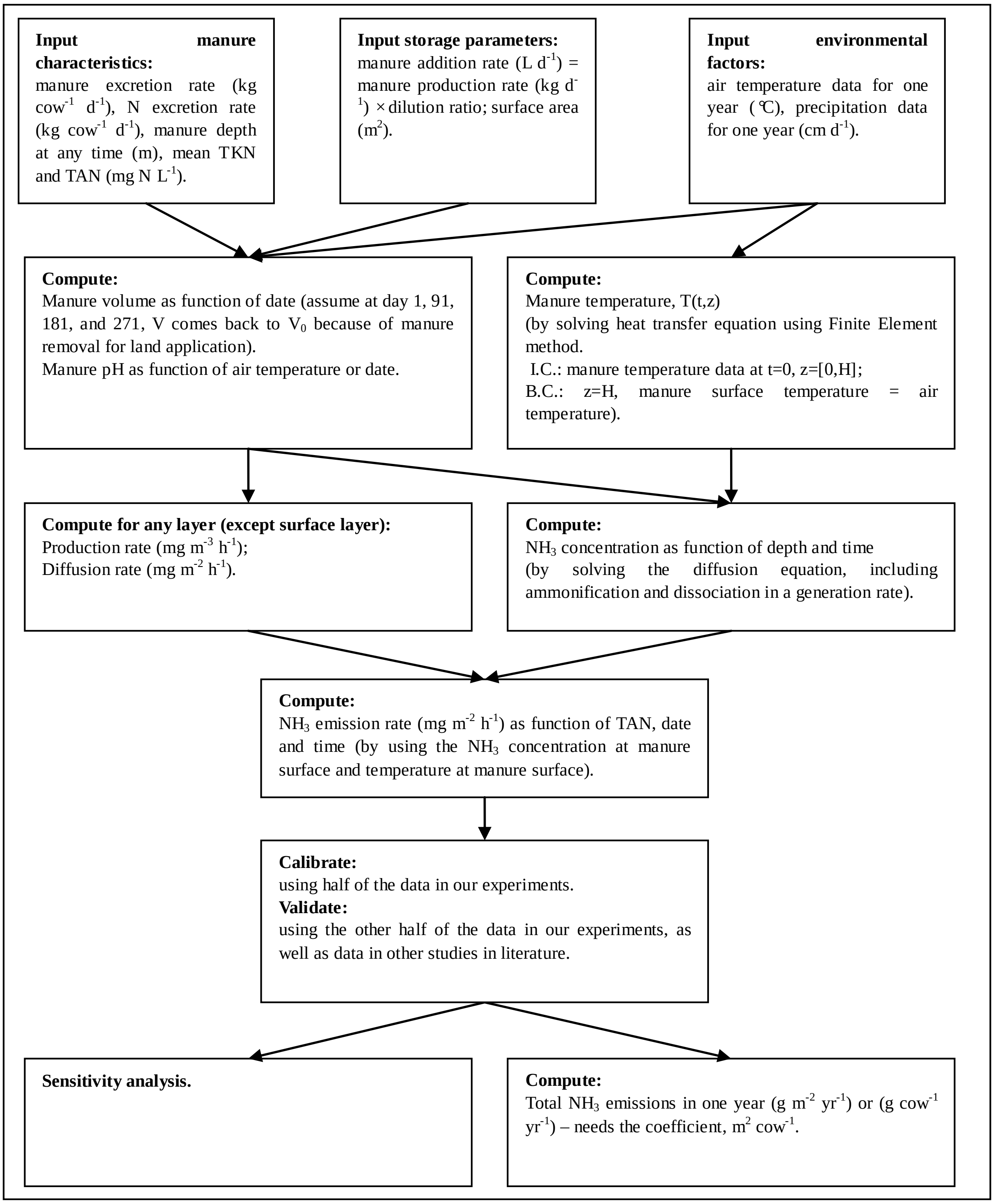

Figure 3-2. Proposed flowchart of modeling ammonia emissions from manure storage

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