AMMONIA EMISSIONS MANAGEMENT AND MODELING FROM STORAGES OF DAIRY MANURE

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AMMONIA EMISSIONS MANAGEMENT AND MODELING FROM STORAGES OF DAIRY MANURE

Abstract

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About 80% of the dairy cattle nitrogen (N) intake is excreted in urine and feces. Urinary-N is ~75% urea while fecal-N is mostly organic. These excretions are either flushed to an anaerobic lagoon or scraped to a manure pit. Estimates indicate that the largest portion (75-80%) of the total-N entering a dairy facility is lost as ammonia (NH_3) from manure storages. Ammonia is a major gaseous pollutant emitted from livestock facilities. Besides its adverse environmental impact, the atmospheric NH_3 can also affect both animal and human health. To manage and regulate NH_3 emissions from animal manure, cost-effective technologies are needed to estimate and mitigate NH_3 emissions.

This research consisted of two parts: In part I, studies were conducted to compare NH_3 emissions between post-collection storages of manure from the two most common dairy manure handling (flush and scrape) systems in the USA. Additional studies were performed to evaluate ammonia emissions mitigation based on urine-feces separation following excretions. In part II, empirical equations of two key components: the overall mass transfer coefficient of NH_3 (K_{oL} of NH_3), and the dissociation constant of ammonium ion (K_d of NH_4^+) were developed to improve a process-based model of NH_3 emissions from open manure storages. Model predictions were validated with measured emissions.

Ammonia emissions fluxes were higher from post-collection storages of scraped manure storages than from storages of flushed manure. Separation of urine and feces did not indicate any advantage over conventional scrape system in the mitigation of ammonia emissions from post-collection storages. The developed non-linear model of K_{oL} of NH_3 as a function of lagoon-liquid temperature (T_L), air velocity (V_{air}), air temperature (T_{air}), and total solids (TS) had a coefficient of determination (R^2) of 0.83. The K_{oL}s increased with T_L and V_{air} but decreased with increase with T_{air} and TS concentrations. The model of K_d of NH_4^+ as a function of T_L and TS concentrations had an R^2 of 0.97. The K_d increased with increase in T_L but decreased with increase in TS. Using these empirical equations, model predicted ammonia fluxes compared well with measured fluxes with a normalized mean error (NME) of 15%.

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Dedication

This dissertation/thesis is dedicated to my Parents

CHAPTER 1

Introduction

1.1 Background

Agricultural activities including concentrated animal feeding operations (CAFOs) account up to 80% of the total anthropogenic ammonia (NH_3) emissions on a global scale (Aneja 2000; Battye et al., 1994). In the US, agricultural activities and livestock operations contribute to about 85% of the anthropogenic NH_3 emissions (EPA 2000). In Europe, about 90% of the anthropogenic NH_3 emissions are believed to be from agricultural activities and livestock operations (Bujjsman et al., 1987). Major pollutants emitted from CAFOs, which have adverse impacts on animal and human health include: carbon dioxide (CO_2), NH_3, nitrous oxide (N_2O), methane (CH_4), particulate matter ($PM_{2.5}$ and PM_{10}), compounds of sulfur (CS), and volatile organic compounds (VOCs).

Ammonia is an atmospheric pollutant which forms sulfate and nitrate aerosols upon reacting with atmospheric sulfuric and nitric acids, respectively, resulting in impaired visibility. Ammonia can volatilize from any component of the CAFOs including animal housing, bedding, solids and liquids separation area, manure storage facilities (under floor pits and anaerobic lagoons), and also from land application of manure (Liang et al., 2002). Impacts of NH_3 emissions range from crop damage, eutrophication of water bodies, environmental acidification, visibility impairment due to haze formation, and odors. Fortunately, NH_3 emissions can be reduced significantly using good manure handling practices (Gay and Knowlton, 2005; de Boer et al., 2002).

In dairy-manure, nitrogen (N) exists in both inorganic and organic forms. Total ammonical nitrogen (TAN), which is inorganic, is the sum of ammonium N (NH_4^+-N) and ammonia N (NH_3-N). In general, only the nitrogen (NH_3-N) species is susceptible to loss via volatilization from dairy wastewater into the atmosphere. Therefore, high levels of NH_3-N in the manure increase the potential of NH_3 volatilization from CAFOs (Sommer et al., 2005; Ni, 1999). In addition, NH_3 emission from manure also reduces its fertilizer value when it is eventually applied on crop-fields or pastures (Sørensen and Amato, 2002). Available data indicate that about 75-80% of the total nitrogen (total-N) entering a dairy facility is lost from an anaerobic lagoon via gaseous emissions (ICL and IDEAL Report, 2005). Even with more conservative estimates of 71% (EPA, 2002) and 50% (AEG USKH Inc., 2005) N loss from anaerobic lagoons, it is clear that these are major sources of NH_3 loss from dairy operations.

Beyond unpleasant odors, extended exposure to NH_3 emission may cause irritations in humans and permanent damage to respiratory tissues of confined animals (Gay and Knowlton, 2005). Ammonia is a precursor to the formation of respirable particular matter ($PM_{2.5}$ aerosol, particulates having aerodynamic diameters $\leq 2.5\ \mu m$). The $PM_{2.5}$ is currently regulated in the USA under the National Ambient Air Quality Standards (NAAQS) (Rumburg et al., 2008). Consequently, it is crucial to evaluate and develop cost-effective methods to mitigate NH_3 emissions from CAFOs so that producers have options to comply with current and future legislations. To set standards for these pollutants, technologies are also needed to estimate their respective concentrations in the air.

1.2 Review of Relevant Literature

1.2.1 Part I: Ammonia Emissions from Post-Collection Storages

The two most common types of manure handling systems in the dairy industry are the flush and the scrape systems (EPA, 2010). In manure-flushing systems, large quantities of water flush animal excreta (urine and feces) along a sloped alley into gutters which then deliver the flushed manure into a storage tank or an anaerobic lagoon. Flushed manure can also be delivered into a pit where it is pumped into storages or other treatment facilities (Figure 1.1). The flushing water is either recycled diluted manure, or fresh water (EPA 2010). In general, flush systems of manure handling need higher initial fixed costs but reduce subsequent labor costs. In addition, research has shown that flushing offers drier floors, and cleaner facilities for the animals (Harner et al., 2005).

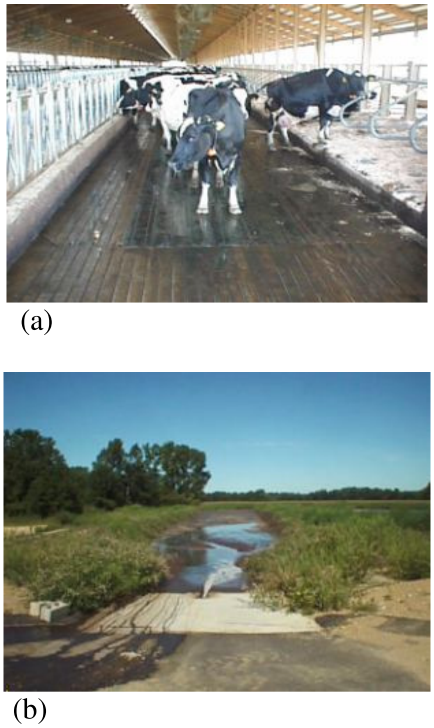

Figure 1.1. Manure flushing system: (a) flushing alley; (b) settling pond/lagoon
(Source: http://www.epa.gov/agriculture/ag101/dairymanure.html)

In the manure scraping systems, on the other hand, either a tractor-mounted scraping blade or an automatically controlled stand-alone scrape-blade is used for manure scraping. With a tractor-mounted scraper, manure is swept from one end of the manure alley to other end (Figure 1.2). In an automatic alley scraping system, a hinged v-shaped chain driven plough continuously or periodically dragged forward to draw manure to the end of an alley (EPA 2010). The scraped manure is usually stored temporarily in solid stacks or loaded directly onto a manure spreader for immediate land application. Available literature indicates that, additional limited flushing of the floors after manure scraping can further mitigate NH_3 emissions inside the barns (Ndegwa et al., 2008; Misselbrook et al., 2006; Braam et al., 1997a).

(a)

(b)

Figure 1.2. Manure scraping systems: (a) Scraping tractor; b) Automatic alley scraper
(Source: http://www.epa.gov/agriculture/ag101/dairymanure.html)

Manure-flush systems in dairies work well and are widely adopted in the US because of labor constraints. Manure-scrape handling systems, in general, are more labor intensive compared to manure-flush systems. There is limited literature available evaluating NH_3 emissions from post-collection storages of scraped and flushed manures. Li et al. (2008) reported that flushed dairy waste management system in closed storages showed 28% less NH_3 loss than scraped system over a 9 week storage period. Furthermore, reported NH_3 emission mitigation studies (Lachance et al., 2005; Stewart et al., 2004; Panetta et al., 2004; Braam et al., 1997a) examined only NH_3 emission mitigations in the barns with respect to these two manure handling systems, but not on subsequent storage of the scraped and flushed manure in anaerobic lagoons. Because these facilities are generally considered responsible for the largest portion of NH_3 loss in a dairy, it is important to understand how the respective manure handling systems during pre-storage affect NH_3 emissions during post-collection storages.

1.2.2 Ammonia Emissions Mitigation via Urine-feces Separation

In ruminants, the conversion of feed-N into milk and meat is an inefficient process and approximately 75-80% of the feed-N intake is excreted in urine and feces. Urinary-N is about 75% urea while fecal-N is mostly undigested organic-N (Tamminga et al., 1994; de Boer et al., 2002). Ammonia can only be released when urinary-N (urea) is hydrolyzed; a process that is catalyzed by enzyme urease present in the feces and not in the urine (Beline et al., 1998). There are two methods of blocking or delaying urea hydrolysis. One method involves use of urease inhibitors while the other method entails segregating urine from feces. Laboratory studies using urease inhibitors (cyclohexylphosphoric triamide (CHPT) and phenyl phosphorodiamidate (PPDA)) which block urease hydrolysis have demonstrated NH_3 emission reductions ranging from 38 to 70% (Varel et al., 1997). This method of mitigating NH_3 emissions requires addition of urease inhibitors to manure slurries at a regular time intervals which may add significant additional expense to CAFO's.

On the other hand, NH_3 emission mitigations ranging from 5% to 99% are reported using urine-feces separation techniques (Lachance et al., 2005; Stewart et al., 2004; Panetta et al., 2004; Braam et al., 1997a). Some of these studies were based on a 100% separation of feces and urine, i.e. totally avoiding any contact between urine and feces, which is not practical; at least not at present time. Nevertheless, even if absolute isolation between urine and feces was achievable, it is still possible that the urease enzyme in ambient air may eventually inhabit urine thus initiating urea hydrolysis.

In the real world, it is very difficult if not impossible to completely eliminate any form of contact between urine and feces. In practice, urine-feces separation has been achieved using one of two methods. The first method uses a sloped conveyor belt that delivers feces to a manure pit. Urine drains down a slope into a separate pit (Lachance et al., 2005; Stewart et al., 2004). The second method uses a floor design which drains urine immediately into a pit after urination. Feces is scraped or washed into a separate storage area (Von Bernuth et al., 2005; Swierstra et al., 2001; Braam et al., 1997a, 1997b). In these scenarios, some of the feces will be carried away by the urine and some of the urine remains on the solid manure. Hypothetically, therefore, the drained urine may have already been inoculated with adequate urease to catalyze urea hydrolysis during post-separation storage. In addition, the urinary urea entrapped in feces also inevitably rapidly hydrolyzes because feces are urease-rich. Some of these questions have not been adequately addressed in previous research. Therefore, there is a need to further examine the urine-feces separation technique especially in regard to mitigation of NH_3 emissions from post-segregation storages. This was one component of the research presented in this thesis.

1.2.3 Part II: Modeling Ammonia Emissions:

Since anaerobic dairy wastewater lagoons account for largest NH_3 emissions in a livestock operation, cost-effective estimations of these emissions are important not only for regulatory purposes but also for implementing NH_3 emissions mitigations strategies from such sources. Direct or actual measurement of NH_3 emissions, however, is difficult, requires expensive instrumentation, and is labor intensive (De Visscher et al., 2002; Liang et al., 2002). An alternative method to estimating NH_3 emissions in a cost-effective way is with process-based emission models.

1.2.4 Structure of the Process Models

Volatilization of NH_3 from manure liquid surface is a function of NH_3 concentration in air $[NH_3]_g$ in the boundary layer in immediate contact with the lagoon liquid surface. The equilibrium of $[NH_3]_g$ with $[NH_3]_L$ is influenced by the Henry's constant (k_H). Ammonia transport rate is governed by the concentration gradient and resistance between the immediate layers of air in contact with the emitting liquid surface (Arogo et al., 1999). A conceptual process diagram of NH_3 release from an anaerobic lagoon is presented in the Figure 1.3. The air (liquid-air interface) immediate to the liquid surface is assumed as a laminar layer. Transfer of NH_3 from liquid surface through this layer is transported by molecular diffusion. Finally, NH_3 transfer from liquid-air-interface into the free air stream occurs by advection (a turbulent layer is assumed) (Sommer et al., 2005).

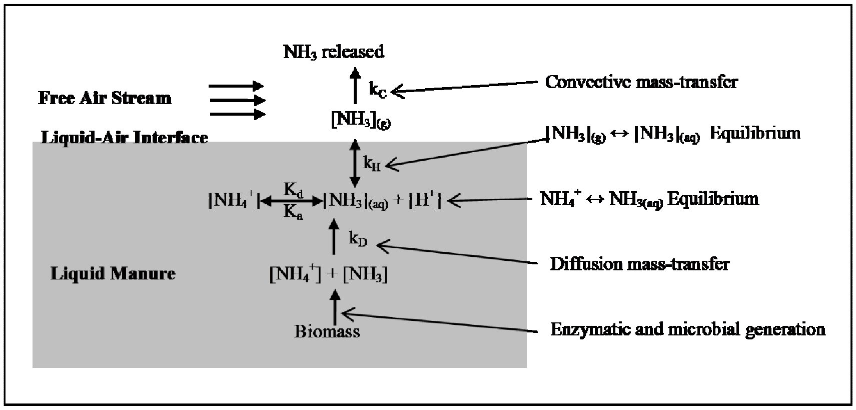

Figure 1.3. Ammonia release mechanism from liquid manure (Ni 1999)

A generic NH_3 emissions process model from bulk liquid from an anaerobic dairy waste lagoon, is presented in Equation [1] (Ni 1999): where: Q_a = Ammonia flux g/s; K_{oL} = Overall mass transfer coefficient, m/s; A = Area of emitting surface, m^2; $[NH_3]_L$ = Free NH_3 concentration at the lagoon liquid surface, g/m^3; and $[NH_3]_a$ = Ammonia concentration in air, g/m^3.

$$Q_a = K_{oL} A([NH_3]_L - [NH_3]_a) \qquad [1]$$

In general, the rate of NH_3 emission is governed by dissociation constant (K_d), diffusion mass transfer (k_D), and convective mass transfer coefficient (k_C). Compared to k_C, the k_D is very small and usually omitted in the NH_3 emission process models. For practical situations $[NH_3]_a$ is generally omitted and Equation [1] be simplified to

$$Q_a = K_{oL} \times A \times [NH_3]_L \qquad [2]$$

The two critical parameters required as inputs in Equation [2] are: the overall mass transfer coefficient (K_{oL}) of NH_3 and the dissociation constant (K_d) of ammonium ion (NH_4^+). The K_{oL} of NH_3 is the desorption rate of free NH_3 from liquid surface into the free air stream, while the K_d of NH_4^+ determines the fraction of the volatile $[NH_3]_L$ in the TAN in the bulk liquid.

1.2.5 The K_{oL} of NH_3

The desorption rate from liquid manure depends on several factors including: liquid TAN concentration, liquid temperature and pH, ambient air temperature, total solids (TS) concentration, and wind speed (De Visscher et al., 2002; Arogo et al., 1999; Ni, 1999). Arogo et al.'s (1999) modeled K_{oL} of NH_3 from an anaerobic under floor swine manure pit using data from a series of laboratory experiments conducted in a convective emissions chamber (CEC). The latter studies showed that the K_{oL} of NH_3 depended on all the three factors that were considered, namely: air flow velocity (V_{air}), lagoon-liquid temperature (T_L), and air temperature (T_{air}). Their model did not consider the effects of suspended solids and ionic strength of the manure on the K_{oL} of NH_3, which other researchers have indicated are significant (De Visscher et al., 2002; Zhang et al., 1994).

Ni (1999) reported empirical values of the K_{oL} of NH_3 from livestock manures in a review paper. However, most of the reported values were for swine lagoon wastewaters and no values were reported for dairy wastewaters. Rumburg et al. (2008), in a more recent study, compared direct measurements of NH_3 emissions with predictions of a process-based model using theoretical and empirical values of the K_{oL} of NH_3 in animal manures reported by Ni (1999). Rumburg et al. (2008) reported that these results indicated significantly wider errors with the theoretically derived K_{oL} values (120% normalized mean error (NME)) compared against empirical values (21% NME). Because theoretical derivations of K_{oL} of NH_3 from livestock wastewaters are inadequate and no empirical K_{oL}s of NH_3 are available for dairy wastewaters (Ni, 1999), an empirical model of the K_{oL} of NH_3 from dairy wastewater is critical for further improvement of NH_3 emissions models.

1.2.6. The K_d of NH_4^+

The K_d of NH_4^+ determines the fraction of the volatile $[NH_3]_L$ in the TAN of the bulk liquid. In general, there is no laboratory or direct method for estimating the proportion of NH_3 in the TAN in aqueous solutions. However, several methods exist to analyze the TAN concentration (APHA 1998). In aqueous solutions, unionized $[NH_3]$ and hydrogen ion $[H^+]$ exist in equilibrium with NH_4^+ as described by Equation [3] (Sommer et al., 2005), which generally depends on the solution temperature and pH. Lowering the liquid pH shifts the equilibrium to the left thus lowering the concentration of NH_3 in the liquid. This is the basic concept behind the methods of using acidification of manure slurries to mitigate emissions of NH_3 or to prevent loss of NH_3 during storage. The dimensionless dissociation constant (K_d) is a function of liquid temperature and liquid pH and free ammonia $[NH_3]_{aq}$ present in the liquid manure. The K_d of NH_4^+ in solution is given by:

$$\left[NH_4^+\right] \leftrightarrow \left[NH_3\right] + \left[H^+\right] \qquad [3]$$

A theoretical model of K_d of NH_4^+ in dilute aqueous solutions only (Arogo et al., 2002), and the corresponding value at 25°C in aqueous solution (Metcalf and Eddy 2003) is presented in Equation [4]. The variation of free NH_3 concentration and NH_4^+ concentration with temperature and pH of the aqueous solution is presented in Figure 1.4 (Loehr, 1974). It shows that with increasing temperature the fraction of NH_3 concentration increases. It also shows that with the increase in pH, the fraction of NH_3 increases and approaches 1.0 at pH higher than 11. This indicates that if the liquid pH is greater than 11, total loss of TAN as NH_3 gas into the air is theoretically possible. Also, the K_d of NH_4^+ in clear water as a function of temperature was computed theoretically from Clausius-Clapeyron Equation by Jayaweera and Mikkelson (1990) as given Equation [5]. Alternatively, Emerson et al., (1975) theoretically modeled the K_d of NH_4^+ in pure water based on the pKa method and obtained Equation [6].

$$K_d = \frac{[NH_3]_{aq}[H^+]}{[NH_4^+]} \equiv 5.62\times10^{-10} \qquad [4]$$

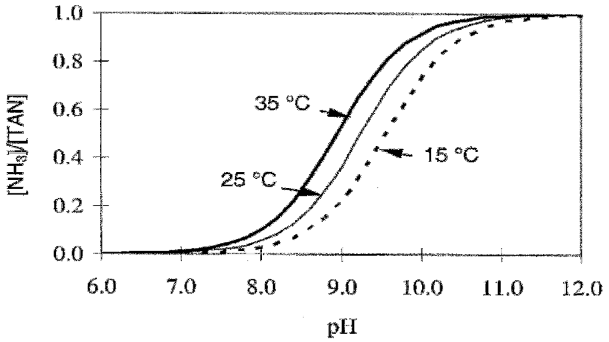

Figure 1.4. Function of NH_3/NH_4^+-equilibrium with temperature and pH in aqueous solutions (Loehr, 1974)

$$K_d = 10^{-(0.0897+2729/T)} \qquad [5]$$

$$K_d = 10^{-(0.09018+2729.92/T)} \qquad [6]$$

A few studies have reported the effect of TS concentrations on the K_d of NH_4^+ in livestock manures (Liang et al., 2002; Arogo et al., 2002; Zhang, 1992; Hashimoto and Lundinton, 1971). The K_d of NH_4^+ in swine manure with 0.25% TS and 400 mg/L TAN at 25°C was about 52% of the value in deionized (DI) water as reported by Liang et al. 2002. The K_d of NH_4^+ in 1% TS-swine manure was about 0.2 times (20%) the K_d of NH_4^+ in water (Zhang, 1992). The K_d of NH_4^+ in chicken manure with 3.5-8.5% TS was about 1/6th (16.7%) of the K_d of NH_4^+ in anhydrous NH_3 solution (Hashimoto and Ludington, 1971). Arogo et al., (2002) reported empirical K_d of NH_4^+ values of swine manure with TS ranging from 0.28% to 0.48% of 0.94, 0.5, and 0.51 compared to K_d of NH_4^+ in pure water at 15, 25, and 35°C, respectively. Lower values of K_d of NH_4^+ with TS have been attributed to the solution ionic strength (Laing et al., 2002), and adsorption of TAN on the solids, which inhibits dissociation (De Visscher et al., 2002). At present, however, majority of the available models estimate K_d of NH_4^+ in livestock manure based on some fraction of K_d of NH_4^+ in pure water.

In summary, the ionic strength is approximated from TDS, while the adsorption of TAN is attributed to the total suspended solids (TSS). The TDS and TSS, in general, constitute the total solids (TS). Therefore, the combined effects of both the TDS and TSS, on the K_d of NH_4^+ in livestock wastewater, are represented by the effects of TS. No empirical study exists in the literature on the combined effect of lagoon liquid temperature, and TS concentrations on K_d of NH_4^+ in dairy manure. Such data would greatly enhance development of process models for estimating NH_3 emissions from dairy wastewaters.

1.3 Research Objectives:

This research is divided into two parts. Part I addresses two critical questions regarding post-collection storages management of manure. Part II focuses on the development of a cost-effective approach for estimating NH_3 emissions from storages of liquid dairy manure. The specific research objectives for each component are outlined below.

Part I: Manure management for mitigating ammonia emissions

1. Evaluation of ammonia emissions from laboratory simulated storages of scraped and flushed dairy manure.
2. Evaluation of ammonia emissions during post-separation storages of separated urine and feces.

Part II: Process-based modeling for estimating ammonia emissions

1. Develop an empirical model of the ammonia overall mass transfer coefficient from liquid dairy manure.
2. Develop an empirical model of the ammonium ion dissociation constant in liquid dairy manure.
3. Collect ammonia emissions data from a full-size dairy wastewater lagoon to validate the ammonia emission process model.

1.4. Dissertation Structure

Each of the following five chapters addresses one of the five specific objectives outlined above. Chapter Two compares ammonia emissions from simulated storages of scraped and flushed manure. An evaluation of ammonia emission mitigation through urine-feces separation is presented in Chapter Three. Chapter Four presents the development of an empirical model of the overall mass transfer coefficient of ammonia in liquid dairy manure. The development of an empirical model of the dissociation constant of ammonium ion in liquid dairy manure is presented in Chapter Five. Chapter Six presents an improved ammonia emissions process model, which incorporates the coefficients developed in Chapters Four and Five. Finally, Chapter Seven outlines the major conclusions drawn from the entire study and offers suggestions for future work.

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CHAPTER TWO

Comparison of Ammonia Emissions from Post-Collection Storages of Scraped and Flushed Dairy-Cattle Manure

2.1 Abstract

Manure scraping and flushing are the two common manure handling systems in concentrated animal feeding operations (CAFOs) in the United States. Previous studies have reported on the impacts of these two manure handling systems on ammonia (NH_3) emissions within barns. There are no studies comparing the impacts of these two manure handling systems on NH_3 emissions during post-collection storages in lagoons and other similar manure storages although these facilities are known to account for the largest portion of NH_3 volatilization in CAFOs. A series of bench scale experiments were conducted for a period of three weeks in controlled laboratory conditions to quantify and compare NH_3 losses from simulated storages of scraped manure and flushed manure based on the exposed-surface-area to volume ratio (ESAVR). Ammonia emission fluxes estimates (with cumulative NH_3 emissions in the parentheses) over a 23-day period were 2.25±0.08g/m^2/day (2034±106.5 mg) from the storage of scraped manure, 2.04±0.04g/m^2/day (1739.3±53.3 mg) from the storage of flushed manure with same exposed surface areas, and 4.62±0.13g/m^2/day (1752±56.3 mg) from the storage of scraped manure with same ESAVR as that of the flushed manure storages. These results indicate that NH_3 emission fluxes from scraped manure storages are at least two times more than from flushed manure storages when both types of manure post-storages have the same ESAVR. However, the cumulative emissions of NH_3 during this period, in descending order, were: Storage of scraped manure (2034±106.5 mg: on the basis of same exposed surface area of the storages); storage of scraped manure (1752±56.3 mg: on the bases of same ESAVR); and the storage of flushed manure (1739.3±53.3 mg).

Keywords: Ammonia, emissions, simulated storage, scrape, manure, flush, post-collection.

2.2 Introduction

Agricultural activities and animal feed operations (AFOs) account for up to 80% of the total ammonia (NH_3) emissions on a global scale (EPA 2002). In Europe, NH_3 emissions from the animal feeding operations (AFOs) and fertilizer applications are believed to be 90% of the total anthropogenic NH_3 release (Bujjsman et al., 1987). Ammonia is an atmospheric pollutant which forms sulfate and nitrate aerosols upon reacting with atmospheric sulfuric acid and nitric acid, respectively, resulting in impaired visibility. Ammonia can be emitted from any part of the AFOs including animal housing, bedding, solids and liquids separation area, manure storage facilities (under floor pits and anaerobic lagoons), and also from land application of manure (Liang et al., 2002). Impacts of NH_3 emissions, in general, ranges from crop damage, eutrophication, environmental acidification, animal and human health, visibility impairment due to haze formation, aerosol formation, and odors. Fortunately, NH_3 emissions can be reduced significantly using good manure handling practices (Gay and Knowlton, 2005; de Boer et al., 2002).

The greatest loss of nitrogen in a livestock operation is due to NH_3 volatilization from anaerobic lagoons, with only about 20-25% of total nitrogen retained in the lagoon liquid being available for fertilizing croplands or pastures (ICL & IDEAL Report 2005). In addition to lowering the fertilizer value of the manure, NH_3 volatilization results in poor air quality which is a global public concern. Previous studies (Ndegwa et al., 2008) have reported on the impacts of manure handling practices on NH_3 emissions within barns but not on the impacts of the handling systems on NH_3 emissions in post-collection storage facilities such as lagoons and scraped manure pits, which are generally considered responsible for the largest portion of NH_3 loss in a dairy.

The two most common types of manure handling systems in the dairy industry are the flushing and the scraping systems (EPA, 2009). In a flushed-dairy system; large quantities of water flush urine and feces excreted by the animals along a sloped alley into gutters that then deliver the flushed manure into a storage tank or a lagoon. The flushed liquid manure can also be delivered into a pumping pit where it is then pumped into storages or other treatment facilities. The flushing water could either be a recycled diluted manure, or fresh water. In general, flush systems of manure handling need higher initial fixed costs but reduce subsequent labor costs. In addition, research has shown that flushing offers dried floors, and cleaner facilities for the animals (Harner et al., 2005).

In manure-scraping systems, either a tractor-mounted scraping blade, or an automatically controlled stand-alone scraping-blade are used for manure scraping. With a tractor-mounted scraper, manure is swept from one end of the manure alley to the other end. In an automatic alley scraping system, a hinged v-shaped chain driven plough continuously or periodically dragged forward to draw manure to the end of an alley. The scraped manure is usually stored temporarily in solid-stacks in a manure pit or loaded directly onto a manure spreader for immediate land application. Available literature indicates that, additional limited flushing of the floors after manure scraping can further mitigate NH_3 emissions inside the barns (Ndegwa et al., 2008). There are no reported studies evaluating NH_3 emissions from post-collection storages of both scraped and flushed manures. The overall objective of this research was to evaluate NH_3 emissions from post-collection storages of scraped and flushed manure in simulated and controlled lab-scale systems to determine potential NH_3 emissions mitigations from adaption of one system over the other.

To achieve the overall objective of this study, the following three experiments were conducted: (i) evaluation of reconstitution of flushed manure from feces and urine, (ii) evaluation of NH_3 emission fluxes from simulated storages of scraped and flushed manures based on similar exposed-surface-area to volume ratios (ESAVR), and (iii) evaluation of NH_3 emissions fluxes from storages of simulated scraped and flushed manures based on similar exposed surface areas of the storages.

2.3 Materials and Methods

The studies as mentioned before were conducted starting with separate feces and urine samples obtained fresh from lactating cows in controlled studies conducted at University of Idaho, Moscow, ID. Fresh fecal samples were collected either from the animal rectum or from the ground while urine samples were obtained by massaging animal vulva. The urine and feces samples were frozen to minimize microbial degradations. Samples were thawed under ambient conditions overnight prior to the commencement of the studies.

A schematic of entire system which was replicated from previous similar studies (Ndegwa et al., 2009, Misselbrook et al., 2005a, Shi et al., 2001) and a photograph of the experimental equipment and instrumentation are shown in Figures 2.1 and 2.2, respectively, while details of manure preparations are given in Table 2.1. This system essentially consisted of a simulated-manure-storage, an acid bottle to trap emitted NH_3, a flow-meter to regulate sweep-air, and a vacuum pump to pull air through the system. Acid sampling for the analysis of the trapped NH_3 was done for every day during first week, every two days during the second week, and every three days during the third week of the experiment. Immediately after sampling, samples were analyzed for TAN concentration using standard methods (APHA, 1992). Each type of manure storage was evaluated in triplicates. The studies were conducted at an average temperature of 17°C. The atmospheric air was drawn using a vacuum pump to sweep NH_3 emissions from the manure surface in each set-up. The air flow rate was controlled at a rate of 1 L/min using a flow meter and a critical orifice. The air carrying NH_3 emitted from the headspace of manure storage was passed through a 150mL 0.2M sulfuric acid contained in 250mL gas wash bottles to trap the emitted NH_3.

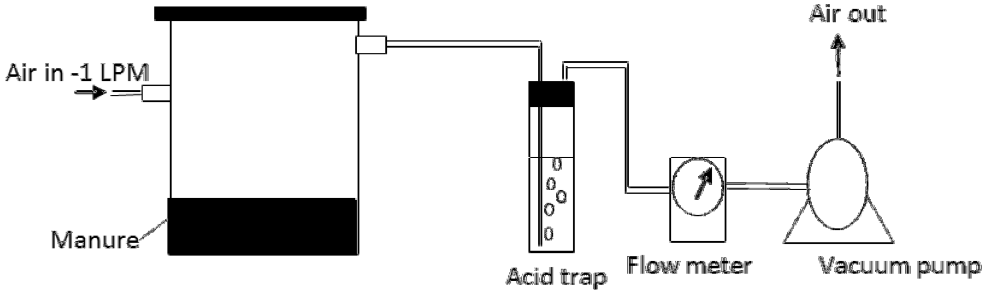


Figure 2.1. Schematic of the set-up used for the study. LPM is liter per minute

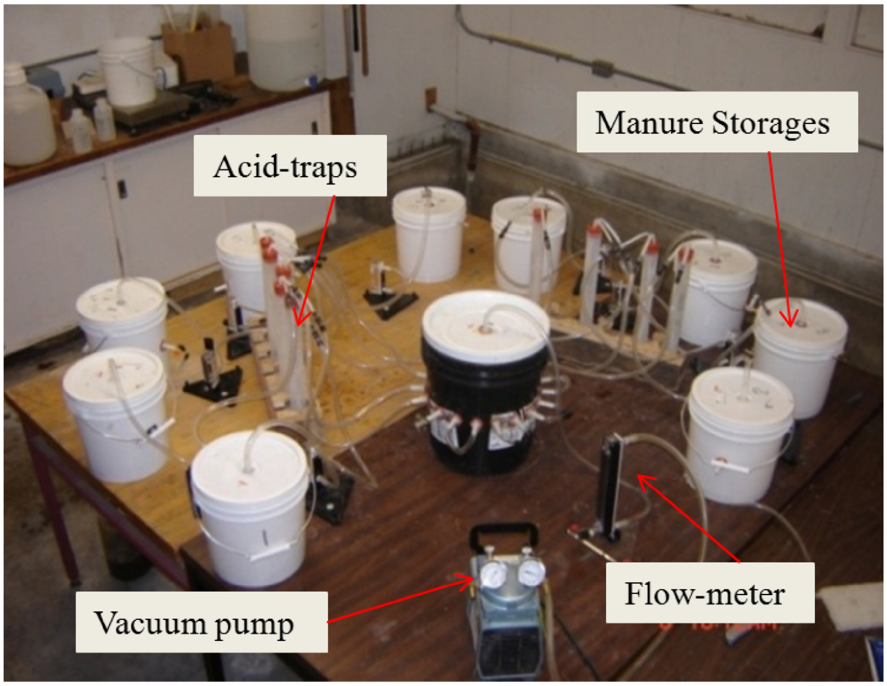


Figure 2.2. A photograph of the laboratory experimental set-up

Table 2.1. Reconstitution of manures from urine and feces for the experiments

	Urine (g)	Feces (g)	Water added (g)	Total wt. (g)
Reconstituted scrape manure	500	840	--	1340
Reconstituted flush manure	500	840	2010	3350
Actual flush manure	--	--	--	3350

Study I: Evaluation of Manure Reconstitution

To objectively compare NH_3 emissions from the respective storages of scraped and flushed manure, it is essential that the source of the manure be similar. The goal of study I was, therefore, to test the reconstitution of flushed manure from the previously and separately collected and frozen urine and feces samples. Thawed samples of urine and feces were mixed in the ratio of 1.0:1.68 that constitutes feces and urine in dairy manure as normally excreted. This ratio is similar to published urine to feces ratios (w/w) ranging from 1.0:1.4 to 1.0:1.9 obtained in lactating dairy cows (Vander Pol et al., 2007 and 2008; Morse et al., 1994). Typical scraped dairy manure has about 6-8% solids. Given scraped manure with 6.25% solids content, this manure can be reconstituted by mixing urine and feces in the ratio of 1.0:1.68 (i.e. urine:feces). The normal range of flushed dairy manure solids content is about 2-3% and thus 2.5% solids content for the flushed manure was used in this study. In this case, flushed manure with 2.5% solids was reconstituted via 2.5 times dilution of the reconstituted scraped manure (6.25% solids) with ordinary tap water. In addition, actual flushed manure which had approximately 2.5% solids content was obtained from a typical commercial dairy for evaluating and comparing the NH_3 emissions with our reconstituted flushed manure. Similar amounts of the actual flushed manure and the reconstituted flushed manure were used in this study to determine NH_3 volatilization from geometrically similar simulated storages. Each of these simulated storages had the same exposed surface area

($411cm^2$) and each storage was evaluated for emissions of NH_3 in triplicate during a period of three weeks.

Study II: Ammonia Emissions from Scraped and flushed manure storages (same ESAVR)

The goal of study II was to determine NH_3 emissions from flushed and scraped manures in post-collection storages based on same ESAVR. Ideally, scraped manure will require less storage than flushed manure. Proportionately, scraped manure would take 2.5 times less storage than flushed manure because of the 2.5 dilution factor, with water, from scraped manure to flushed manure. Flushed manure and scraped manure were reconstituted as in study I from separate urine and feces samples and ordinary tap water. The post-collection storages of reconstituted flushed manure and the scraped manure were simulated in two different storages each providing approximately an ESAVR of $123cm^2/kg$ of either reconstituted flushed manure or scraped manure.

Study III: Ammonia Emissions from Scraped and flushed manure storages (same exposed surface area)

The goal of study III was to estimate and compare NH_3 emissions from scraped and flushed manures in the post-collection storages based on the same exposed surface areas. The assumption here was that both the scraped and flushed manures will be stored in geometrically similar post-collection storages. This unlikely scenario is likely to occur if a producer converted from a flushing system to a manure scraping system but then decides to continue using the old storage facility with modifications. For this study, flushed and scraped manures were reconstituted as in study I from separated fresh urine, feces, and tap water. Equivalent amounts of flushed and scraped manures; 3350g reconstituted flushed manure, and 1340g of reconstituted scraped manure were each placed in respective storages with similar geometry (same exposed surface area of 411cm^2). Each reconstitution was made in triplicate and conducted for three weeks.

2.4 Data Analysis

Ammonia emissions from the respective post-collection storages were evaluated based on: (i) total cumulative NH_3 emissions, and (ii) ammonia emissions fluxes (mg/day/m^2). Emission fluxes were computed from the respective daily NH_3 emission rates (slopes of the linear regression plots) and the known exposed surface areas of the corresponding storages. An ANOVA was performed on the treatment means using SAS (SAS Institute Inc, 2003) at the significant level of $\alpha=0.05$. If the results of ANOVA indicated significant differences amongst the treatment means, multiple pair-wise comparisons were performed using the Duncan's multiple range-test to separate the means.

2.5 Results and discussion

Study I: Testing of the Simulated Flushed Storage System

The goal of this study was to test the reconstitution of flushed manure from separate urine and feces samples. The daily cumulative NH_3 emissions from simulated storages of reconstituted flushed manure and actual flushed manure with same exposed surface areas are shown in Figure 2.3, while total cumulative NH_3 emissions during the three weeks of evaluation are presented in the Table 2.2. The results of ANOVA indicate the cumulative NH_3 losses from these two manure storages were not significantly different (P-value = 0.98, referred to as P hereafter). With respect to NH_3 emissions fluxes, however, the results of ANOVA also indicated that the emissions fluxes were not significantly different (P = 0.24). Based on these analyses, there is no evidence indicating that the reconstituted flushed wastewater was different from the actual flushed wastewater. These results thus validate all the assertions made during reconstitution of flushed manure from urine, feces, and tap water.

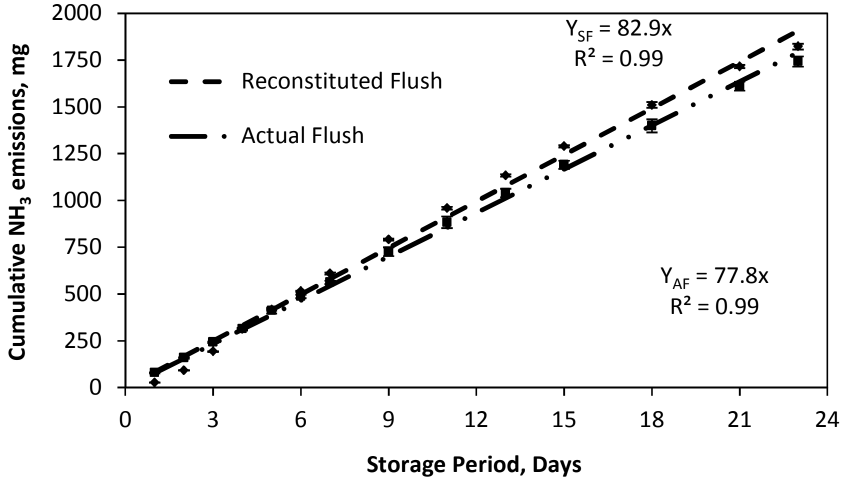


Figure 2.3. Cumulative ammonia loss from reconstituted and actual flushed manure storages with same exposed surface areas (error bars indicate standard deviation from mean)

Table 2.2. Total ammonia losses (mean± standard deviation) from the post-collection storages of manures at the end of the experiments

Scrape manure[‡] (mg)	Scrape manure[†] (mg)	Flush manure[‡†] (mg)
1752±56.3[a*]	2034±106.5[b]	1739.3±53.3[a*]

*Means with the same letter are not different significantly at α=0.05

[†] Means same exposed surface area

[‡] Means same exposed-area-to-volume-ratio

Study II: Ammonia Emissions from Scraped versus Flushed Systems (same ESAVR)

The goal of this study was to compare cumulative NH_3 emissions and NH_3 emission fluxes from simulated storages of flushed and simulated scraped manures based on the same ESAVR. The plots of cumulative NH_3 losses from simulated storages of scraped and flushed manures with same ESAVR are given in Figure 2.4. The slopes from the plots (82.9 mg/day (simulated storage of flushed manure) and 84.5 mg/day (simulated storage of scraped manure) were analyzed with 1-way ANOVA for similarities and/or differences. The results of ANOVA, the cumulative NH_3 losses from these two types of storages were not significantly different (P = 0.80). The NH_3 emission fluxes from the scraped manure storage, however, were significantly higher ($P < 0.05$) than from the flushed manure storage. The significantly higher NH_3 flux from the scraped manure storage explains the insignificant difference of cumulative NH_3 losses from the storages of either type of manure. Based on these results, we can infer that, there is no significant difference in NH_3 loss during post-collection storages of either scraped, or flushed dairy manure if the same ESVAR is maintained in the respective storages. Since previous research has indicated that manure flushing mitigates NH_3 emissions more than manure scraping, we can infer that: manure flushing from barns is superior to manure scraping in the overall mitigations of NH_3 emissions in CAFOs.

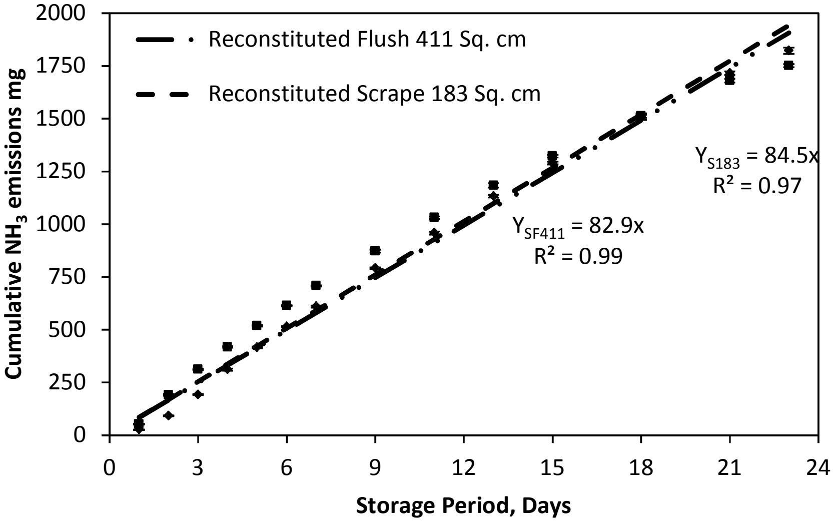


Figure 2.4. Cumulative ammonia loss from storages of scraped and flushed manures (error bars indicate standard deviation from mean)

Study III: Ammonia Emissions from Scraped versus Flushed Systems (same **Exposed Surface Area)**

The goal of this study was to evaluate cumulative emissions of NH_3 and NH_3 fluxes from simulated storages of flushed and scraped manures disregarding the importance of ESAVR. The assumption in this study was that a flushing system was replaced with a scraping system and the storage facility used previously for the flushed manure is used for the scrape manure. The plots of cumulative NH_3 loss from the simulated storages of scraped and flushed manures are presented in Figure 2.5. The slopes from the plots (92.6 mg/day (storage of scraped manure) and 82.9 mg/day (storage of flushed manure) were analyzed with 1-way ANOVA for similarities and/or differences. The results of ANOVA indicate that both the cumulative NH_3 losses ($P = 0.013$) and the NH_3 emission fluxes ($P = 0.013$) from the storages of scraped and flushed manures were significantly different. From these results, we infer that, for geometrically similar storages (with respect to exposed surface areas), post-collection storage of scraped manure will result in significantly higher NH_3 losses as well as significantly higher NH_3 fluxes than the storage of flushed manure; within the first three weeks of storage examined in this study.

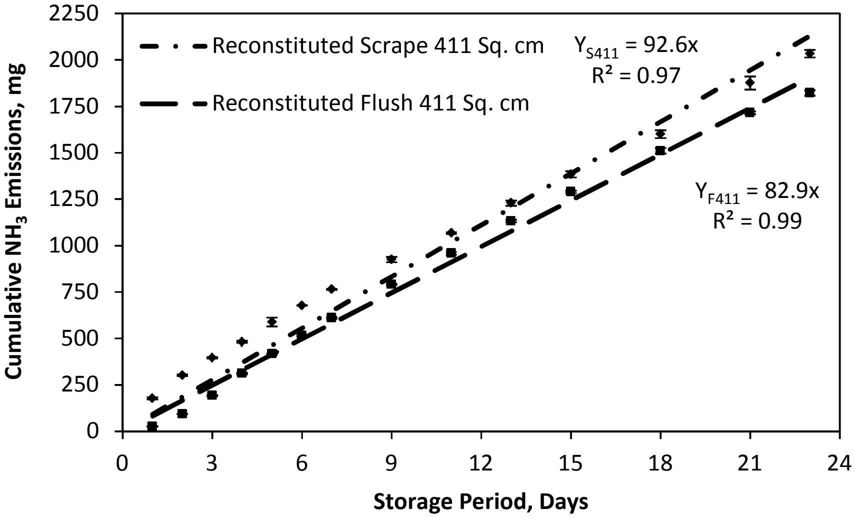
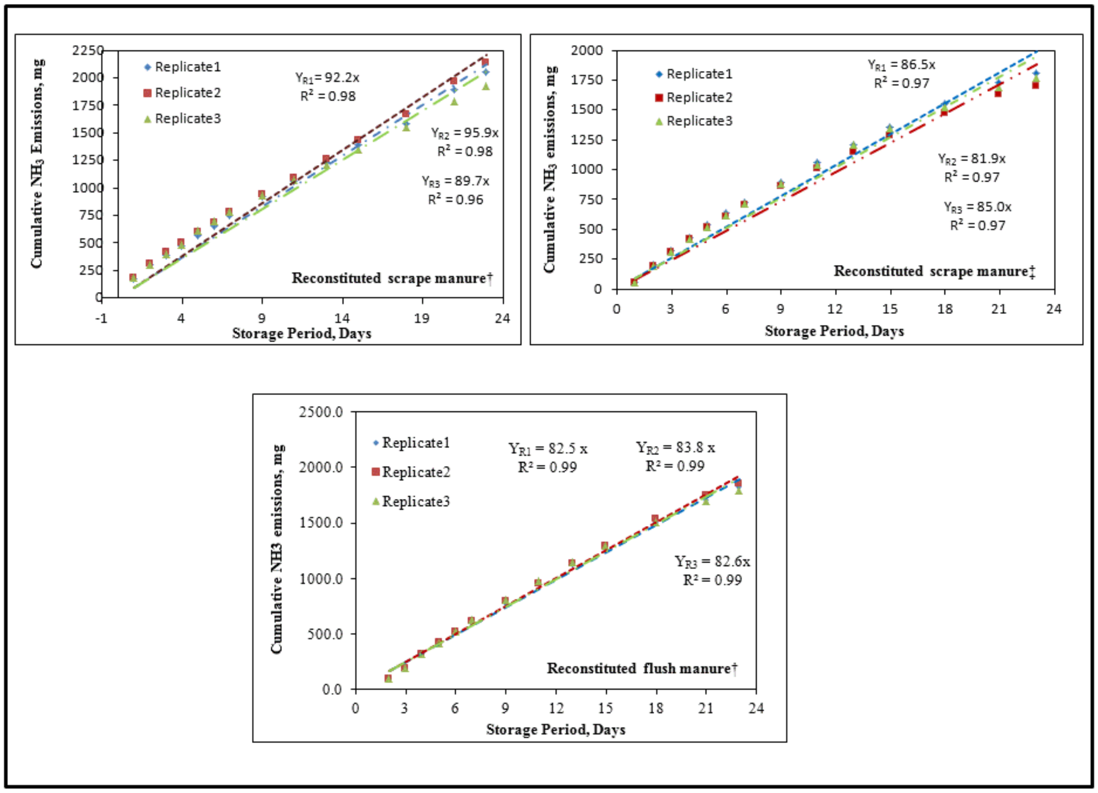


Figure 2.5. Cumulative ammonia loss from simulated storages of scraped and flushed manures with the same exposed surface areas (error bars indicate standard deviation from mean)

In addition to individual data analyses of the preceding three studies, this paper also further examined data from all three studies together. Graphs of cumulative NH_3 loss and linear regressions of emissions from simulated storages of scraped manure (based on same ESAVR), scraped manure, and flush manure (based on same exposed surface areas) are shown in Figure 2.6 and emission fluxes from these three storages are given in Table 2.3. In general, the emissions from all three simulated storages showed similar and linear trends as indicated by the strong coefficients of determination (R^2) values ranging from 0.96 to 1.00. From Table 2.3, the results of ANOVA indicated that fluxes from simulated storages of scraped manure (based on same ESAVR), scraped manure, flushed manure (same exposed surface area) were statistically significantly different (P = 0.005). Multiple pair-wise comparisons of the means showed significantly higher fluxes from storage of scrape manure (same ESAVR as that of flushed manure storage); followed by, storage of scraped manure, and storage of flushed manure (same exposed surface area as that of flushed manure storage), respectively.



†Means same exposed surface area
‡Means same exposed-area-to-volume-ratio

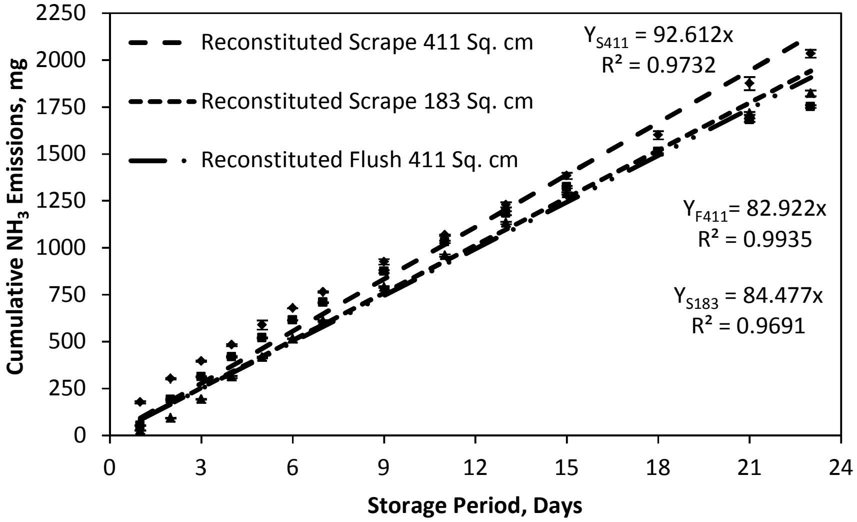
Figure 2.6. Linear regressions plots of cumulative ammonia emission losses from each manure storage

Table 2.3. Ammonia emission fluxes (mean± standard deviation) from simulated post-collection storages of dairy manure

Manure storage type	Flux (g/day/m^2)
Scraped manure (same ESAVR)	4.62 ± 0.13^a
Scraped manure (same exposed surface area)	2.25 ± 0.08^b
Flushed manure (same exposed surface area)	2.04 ± 0.04^c

[a,b,c] significantly different with each other at $\alpha=0.05$

A plot of linear regression analyses of the average cumulative NH_3 losses from manure storages is presented in Figure 2.7. The ANOVA of the cumulative NH_3 losses from these respective storages similarly indicated significant differences in the cumulative NH_3 losses (P = 0.018). Duncan's multiple comparison indicated that the cumulative NH_3 loss from the storage of scraped manure (with the same exposed surface area as that of the flushed manure storage) were significantly higher than that from either the storages of scraped manure (with the same ESAVR as the flushed manure) or the storage of flushed manure.



[†]Means same exposed surface area
[‡]Means same exposed-area-to-volume-ratio

Figure 2.7. Linear regression curves of cumulative NH_3 losses from manure storages (error bars indicate standard deviation from mean)

In general, NH_3 emission fluxes from the post-collection storages of the scraped manure were apparently higher than that from flushed manure storages. The NH_3 fluxes from our simulated storages of flushed manure (1.9 – 2.0 $g/m^2/day$) compared well with previously reported NH_3 fluxes from lagoons and other storages of dairy-flushed wastewaters. In a field study, Rumburg et al. (2008) reported NH_3 fluxes ranging between 2.6 and 13 $g/m^2/day$. Other studies by Smith et al. (2007) at both pilot and field scales reported NH_3 fluxes ranging from 1.0 to 7.6 $g/m^2/day$. From their field studies McGinn et al. (2008) reported NH_3 emission fluxes ranging from 3.6 to 8.6 $g/m^2/day$. However, NH_3 emission fluxes averaging 0.03±0.013 $g/m^2/day$ in winter at an average temperature of 6.6°C and 1.13±0.19 $g/m^2/day$ in summer at an average temperature of 29°C from the field studies using a dynamic chamber method from two anaerobic dairy lagoons reported by Mutlu et al. (2004) do not agree with the results of our simulated laboratory studies. In general, the fluctuations of environmental conditions under which Rumburg et al. (2008), McGinn et al. (2008), Smith et al. (2007), and Mutlu et al. (2004) field and pilot studies were conducted compared to our controlled laboratory conditions explain some of the observed discrepancies.

2.6 Summary and Conclusions

A series of laboratory studies were conducted to evaluate NH_3 losses from simulatied post-collection storages of dairy manure from two common manure handling systems found in the US: manure flushing and scraping. The conclusions from the results of these studies are:

1. The cumulative NH_3 losses and NH_3 fluxes from simulated storages of flushed manure and actual flushed manure were not significantly different at $\alpha=0.05$. The assertions (diluting a mix of urine to feces in the ratio of 1.00:1.68 with 2.5 times tap water on weight basis)

made for reconstitution of flushed manure from separately collected urine and feces were, therefore, valid.

2. The cumulative NH_3 emissions and NH_3 fluxes from simulated storages of scraped and flushed manure with same exposed-surface-area to volume ratios were not statistically different at $\alpha=0.05$. This result indicates no advantage of either scraping manure or flushing manure if the designs of the storages of flushed and scraped manure are based on the same ESAVR.
3. Emissions of NH_3 from post-collection storages of flushed and scraped manure in similar storages (based on same exposed surface area) indicated statistically significantly different emissions at $\alpha=0.05$. Ammonia emission from the storage of scraped manure was higher than that from storage of flushed manure. The results infer that if scraped and flushed manures ended up in geometrically similar manure post-collection storages, higher NH_3 emissions would be experienced from the storage of scraped manure.

2.7 Acknowledgements

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CHAPTER THREE

Ammonia Emissions from Post-Collection Storages of Separated Dairy Cattle Excretions

3.1 Abstract

About 80% of dairy cattle N intake is excreted as urine and feces. Urinary-N is about 75% urea and fecal-N is mostly organic. Ammonia (NH_3) can only be volatilized when urinary urea is hydrolyzed by the urease enzyme present in the feces (urease is not present in the urine). Minimizing contact between urine and feces may thus be an effective approach to reducing urea hydrolysis and thus subsequent NH_3 emissions. Indeed, previous studies have reported 5 to 99% NH_3 emissions mitigation within barns through separation of feces and urine. The objective of this study was to compare NH_3 emissions mitigation via separation of urine and feces in post-collection storages against a conventional scrape manure handling method where urine and feces are comingled. Laboratory scale simulation studies were conducted to evaluate NH_3 emissions from post-collection storages of three waste streams: i) idealistically separated feces and urine (no contact between urine and feces), ii) realistically separated urine and feces, and iii) conventionally scraped manure. From results of these studies, NH_3 losses ranking in descending order were: aggregate of idealistically separated waste streams, aggregate of realistically separated urine and feces, and the scrape manure, respectively. Based on the results of our studies, therefore, the extra effort of separating the waste streams would not enhance mitigation of NH_3 losses from post-collection storages of the separated waste streams compared to the conventional scrape manure collection system.

Keywords: Ammonia emissions, simulation, scrape, manure, urine, separation, ammonia traps.

3.2 Introduction

Major pollutants emitted from concentrated animal feeding operations (CAFOs) such as dairies that have adverse impacts on health and quality of life include: carbon dioxide (CO_2), ammonia (NH_3), nitrous oxide (N_2O), methane (CH_4), particulate matter ($PM_{2.5}$ and PM_{10}), compounds of sulfur (CS), and volatile organic compounds (VOCs). Emission of NH_3 from livestock operations is of particular concern because of its broader adverse environmental impacts. Impacts of NH_3 emissions range from crop damage, odors, eutrophication, decreased animal and human health, and impairment of visibility due to the formation of aerosol haze. Available data indicate that CAFOs and agricultural activities, in general, locally and globally contribute about 80% of total NH_3 emissions (EPA 2002, Liang et al., 2002; Aneja et al., 2000; Sommer et al., 1995; Battye et al., 1994). Ammonia emissions in Europe from CAFOs and agricultural fertilizer application are estimated to be 90% of total anthropogenic NH_3 emissions (Bujjsman et al., 1987). Similarly, NH_3 emissions in Asia from the CAFOs and agricultural fertilizer applications account for 77% of total anthropogenic NH3 emissions (Zhao and Wang, 1994). In the US, production of NH_3 is currently being legislated under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Emergency Planning & Community Right-to-Know Act (EPCRA). It is likely that NH_3 (as a secondary source of $PM_{2.5}$) may soon be regulated under the Clean Air Act (Ndegwa et al. 2008). Consequently, it is crucial to evaluate and develop cost-effective methods that producers can choose from to mitigate NH_3 emissions from CAFOs in order to comply with current and future legislations.

In ruminants, the conversions of feed-N into milk and meat are inefficient processes and approximately 75-80% of the feed-N intake is excreted in urine and feces. Urinary N is about 75% urea while fecal N is mainly in the form of undigested organic nitrogen compounds (Tamminga et al., 1994; de Boer et al., 2002). Ammonia can be emitted at any point in CAFOs including: animal housing, solids-liquids separation units, manure storage facilities (under floor pits and anaerobic lagoons), and from manure application (for soil amendment) sites (Liang et al., 2002). Many approaches to mitigate NH_3 emissions have been proposed including: urine-feces separation, reducing manure pH, NH_3 binding, biological treatments, appropriate building designs and manure management, emissions capture and treatment with filters and bio-filters, and land application strategies (Ndegwa et al. 2008). This research work further examined the urine-feces separation technique in regard to mitigation of NH_3 emissions from post-collection storages.

Ammonia can only be volatilized when urinary urea is hydrolyzed by the enzyme urease which is present in the feces and not in the urine (Beline et al. 1998). Laboratory studies have shown that the addition of urease inhibitors such as cyclohexylphosphoric triamide (CHPT) and phenyl phosphorodiamidate (PPDA) which block urease hydrolysis can be used to reduce NH_3 emissions by 38 to 70% (Varel et al., 1997). However, this method of NH_3 emissions control requires addition of urease inhibitors to manure slurries at regular time intervals. Because urea is only found in urine and the enzyme urease that hydrolyzes urea to NH_3 is only found in feces, it may be hypothesized that avoiding contact between feces and urine after excretion of each would mitigate NH_3 emissions from such excretions. Past studies have reported that reduction of NH_3 emissions ranging from 5% to 99% can be achieved by the separation of urine and feces in barns (Lachance et al., 2005; Stewart et al., 2004; Panetta et al., 2004; Braam et al., 1997a). Some of these studies were based on an 'ideal' separation of feces and urine or 100% no contact between urine and feces.

It is important to point out that, even if absolute isolation between urine and feces is achieved, it is still possible that the urease enzyme in ambient air may inoculate urine. In real life, it is very difficult if not impossible to completely eliminate any form of contact between urine and feces. In the field, urine-feces separation has been achieved using one of two methods. The first method uses a sloped conveyor belt that delivers feces to a manure pit. Urine flows down a slope into a separate pit (Lachance et al., 2005; Stewart et al., 2004). The second method uses a floor design that drains urine immediately into a pit after urination. Feces is scraped or washed into a separate storage area (Von Bernuth et al., 2005; Swierstra et al., 2001; Braam et al., 1997a, 1997b). There is no research on NH_3 emissions from post-separation storages of the separated urine and feces. This study addressed two important questions: (i) how much NH_3 emission mitigation could be achieved in realistic separation of feces and urine as opposed to idealistic separation, and (ii) how long it would take the separated urine to start emitting NH_3 even in situations of idealistic separation given the fact that urine urea may also be hydrolyzed by urease enzyme indigenous in the environment.

In realistic separation of urine and feces, the animal usually excretes a pile of feces on the ground followed most often by urination over feces pile. The urine then drains away from feces. In this scenario, some of the feces will be carried away by the urine and some of the urine remains on the solid. Hypothetically, therefore, the drained urine may have already been inoculated with the urease enzyme which accelerates urea hydrolysis during post-separation storage. On the other hand, the urea in the urine entrapped in the feces will also inevitably hydrolyze rapidly. In the idealistic separation of urine and feces, urine and feces are collected directly after excretion from the animal without contact. Hypothetically, therefore, there should be minimal loss of NH_3 from both urine and feces during separate post-collection storages in the latter approach.

3.3 Materials and methods

The average daily ratio of feces and urine excreted by the animal is 1.0:1.68 on weight basis, which translates into a total solids concentration of approximately 6.25% (on weight basis) in scrape manure. To reconstitute scrape manure with 6.25% solids from urine and feces collected separately, 1000 g of urine and 1680 g of feces were mixed. To simulate realistic separation of urine and feces, about 2.0 kg urine was discharged over 3.36 kg of feces (1.0:1.68 ratio) placed on an inclined pan. Urine was made to run from a height of 1.25 m (average cow height) on the fresh feces placed on a pan to simulate real situations of how cow excretes urine over feces (Figure 3.1). The inclined pan drained the urine away towards the lower end where the urine was collected into one container. The feces remaining on the pan was collected into another container. Exactly 500 g separated urine was placed into a 2 gallon bucket and the bucket was sealed. Exactly 840 g of the separated feces was placed into another 2 gallon bucket, which was also sealed. Idealistically separated urine (ISU) and feces (ISF) were placed in separate containers. Each of these simulations was evaluated in triplicates in controlled laboratory conditions for the respective NH_3 emissions over a three-week duration.

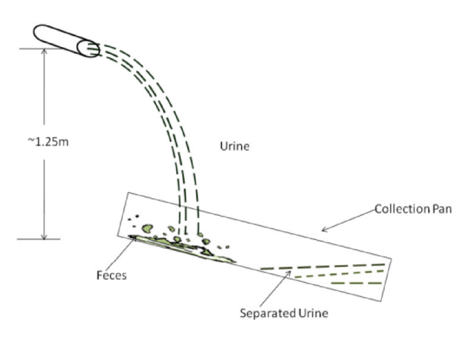

Figure 3.1. Simulation of urine-discharge from a typical cow (representing realistic urine-feces separation)

A schematic of the laboratory system used to simulate storage of the post-separated urine and feces, and scraped manure is presented in Figure 3.2. The atmospheric air was drawn using a vacuum pump to sweep the NH_3 emissions from the manure surface in each system. The air flow rate was controlled at a rate of 1 L/min using a flow meter and a critical orifice. The air with NH_3 emitted from the manure surface was passed through a 150 mL 0.2 M sulfuric acid contained in 250 mL gas wash bottle to trap the emitted NH_3. Acid trap details were adopted from previous similar studies (Ndegwa et al., 2009, Misselbrook et al. 2005a, Shi et al. 2001). This system consisted of a simulated-waste-storage, an acid bottle to trap the emitted NH_3, a flow-meter to regulate sweep-air, and a vacuum pump to pull air through the system. Acid sampling for the analysis of the trapped NH_3 concentration was done for every 24 hours for first seven days and 2-days once over the 2^{nd} week, and 3-days once over the 3^{rd} week of the experiment. Immediately after sampling, samples were analyzed for total ammonia nitrogen (TAN) concentration using standard methods (APHA 1992).

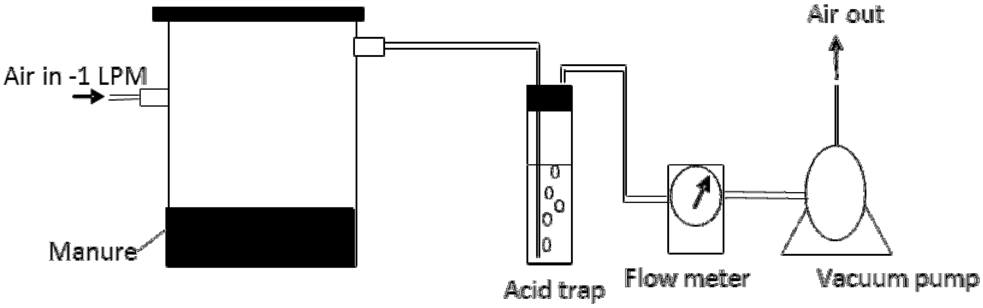

Figure 3.2. Schematic of the simulated post-collection storage systems used in our studies

3.4 Data Analysis

Ammonia losses data analyses from the respective post-collection storages were done for both short-term (up to 14 days) and long-term (23 days) periods. Short-period analyses were to determine if (and when) ISU would start releasing NH_3 from inoculation of urease enzyme from the environment. Linear regressions were performed on each of storages against cumulative NH_3 emissions with variation of time. Ammonia emission rates were compared for the consistency of NH_3 emissions from the waste streams of realistically separated urine (RSU) and realistically separated feces (RSF), ISU and idealistically separated feces (ISF), and scraped manure. Long-term analysis was intended to analyze whether ISU and ISF would mitigate NH_3 emissions better than either the RSU and RSF, or the scraped manure in the post-collection storages. Details of cumulative average NH_3 losses from replicates with respective standard deviations from storages of waste streams for a period of 23 days are given in the Table 3.1. The NH_3 emissions were obtained by adding for the whole period average daily NH_3 emissions from the respective replicates. The ISF, RSF, RSU, and scraped manure (in Table 3.1) were the mean of three replicates, while ISU was the mean of two replicates.

Table 3.1. Average Cumulative NH_3 losses from the waste streams for 23 days

	ISF	RSF	ISU	RSU	Scrape manure
Cumulative NH_3 loss, mg	76.1±0.4	552.0±44.3	2971±738	2898.0±88.0	2034.0±106.5

ISF: Idealistically separated feces; RSF: Realistically separated feces; ISU: Idealistically separated urine; RSU: Realistically separated urine

3.5 Results and Discussions:

Details of the characteristics (total solids, TS; total volatile solids, TVS; pH; total ammonical nitrogen, TAN; and total Kjeldahl nitrogen, TKN) of the urine, feces, RSF, RSU, and ISU at the beginning and at the end of the studies are given in the Table 3.2. At the beginning of the experiment, TAN in the ISU and feces were low because as noted earlier nitrogen in feces is mostly organic while most nitrogen will be urea in the urine before hydrolysis into ammonical nitrogen upon feces-urine contact. It is also evident that at the end of the studies, the TAN contents in RSF, RSU, and ISU were much lower than at the beginning of studies because of NH_3 loss from the respective storages. Comparing TAN at the beginning (4809 mg) and at the end (2029 mg) in the scrape manure storage, a large fraction of potentially volatile TAN was still available at the end of the study. From the results presented in Table 3.2, TAN loss from the feces stream was minimal (76mg) during the 3-week post-collection storage, while about 67% of the initial TKN remained in feces at the end of the three-week study-period. This is probably because the mineralization of organic N in the feces would take a longer time to convert into TAN.

Table 3.2. Characteristics of the various waste streams at the beginning and end of the study period

	Initial					End				
Character	RSF	RSU	ISU	ISF	Scrape	RSF	RSU	ISU	ISF	Scrape
TS (%)	17.3	5.7	4.1	19.8	13.5	19.7	8.8	6.2	28.6	14.4
TVS (%)	14.8	8.02	0.85	17.1	11.1	16.83	5.23	1.9	22.6	11.4
pH	7.4	8.2	8.7	6.4	8.2	7.9	9.7	10.0	6.3	7.2
TAN (mg)	1183	1506	219	256	4803	273	30	9	237	2029
TKN (mg)	5612	3670	4018	4136	10796	3716	611	591	2756	6605

Short term studies

The results of NH_3 emissions from the respective storages of RSF, and the scrape manure during the first 48 hours after excretion are shown in Figure 3.3. Assuming that in a typical scrape dairy manure scraping from the barn is done at least every 24 hours, it is evident from these results that if the barn is designed to drain urine from the floors to the outside of the barn or the animal housing, the feces (and any urine entrapped in the feces) remaining on the floors would release much less NH_3 than if the urine was not drained away (i.e. conventional scrape system). From the results of this study, draining urine away from feces within the barn can potentially reduce NH_3 emissions within the barn by approximately six-fold compared to the conventional scrape manure collection system. Therefore, based on these results, it can be inferred that draining urine from the floors of barns immediately after excretion enhances mitigation of NH_3 emissions compared to the conventional scrape system. This supports previous studies on NH_3 mitigation within enclosed animal housing via urine-feces separation (von Bernuth et al., 2005; Panetta et al., 2004; Swierstra et al., 2001; Braam et al., 1997a, 1997b).

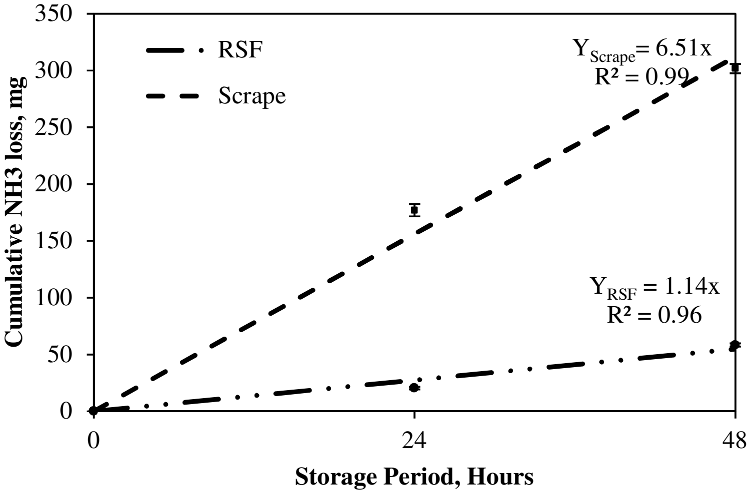

Figure 3.3. Ammonia emissions from realistically separated feces (RSF), and conventional scrape manure in the first 48 hours after excretion (error bars indicate standard deviation from mean)

Ammonia emissions from the storages of RSU and RSF during the first seven days of storage are shown in Figure 3.4. Evidently, NH_3 emissions within this duration increased linearly with time as manifested in the high correlation coefficient (R^2) of 0.99. It can thus be inferred that the daily rates of NH_3 emissions from the two storages in the first week were constant. Within this first week of monitoring, the rate of NH_3 emission from the RSU was more than nine times higher than that of the rate of NH_3 emission from the RSF. This significantly larger rate of NH_3 loss from the RSU could be the result of hydrolysis of urinary urea by urease enzyme inoculated in urine from the feces during the initial feces-urine contact. On the other hand, NH_3 losses from the RFS within this duration may be attributed to the hydrolysis of trace urinary urea that could have been entrapped in the feces while the rest of urine drained away.

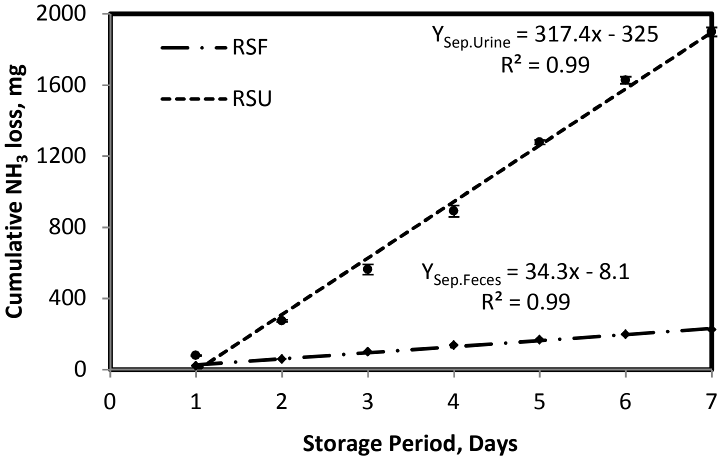

Figure 3.4. Ammonia emissions within the first week from simulated storages of realistically separated urine (RSU) and realistically separated feces (RSF) (error bars indicate standard deviation from mean)

Profiles of cumulative NH_3 losses from storages of aggregate of realistically separated urine and feces (RSUF) and scrape manure for the first seven days of post-separation storages are given in Figure 3.5. Aggregate NH_3 loss from separate storages of RSU and RSF (loss from RSU + loss from RSF) was much higher than the NH_3 loss from the storage of scraped manure. The rate of NH_3 loss from the storages of RSUF was approximately 3.5 times higher than the loss from storage of scraped manure. It is quite apparent that the higher aggregate loss from the storages of RSU and RSF comes from the storage of separated urine, which is also even individually higher than the loss from the storage of the scrape manure. A possible explanation to this observation is that probably the fecal solids material reduces the NH_3 mass transfer characteristics of NH_3 from liquid into air thus inhibiting NH_3 release from the scrape manure storage. In past research work, the dissociation constant (K_d) of ammonium ion (NH_4^+) in dilute finishing swine manure with 1% total solids (TS) and in concentrated chicken manure slurries have respectively been reported being one-fifth and one-sixth that of

K_d of NH_4^+ in water (Zhang et al. 1994; Hashimoto and Ludington, 1971), indicating possible effects of TS on the eventual ammonia loss.

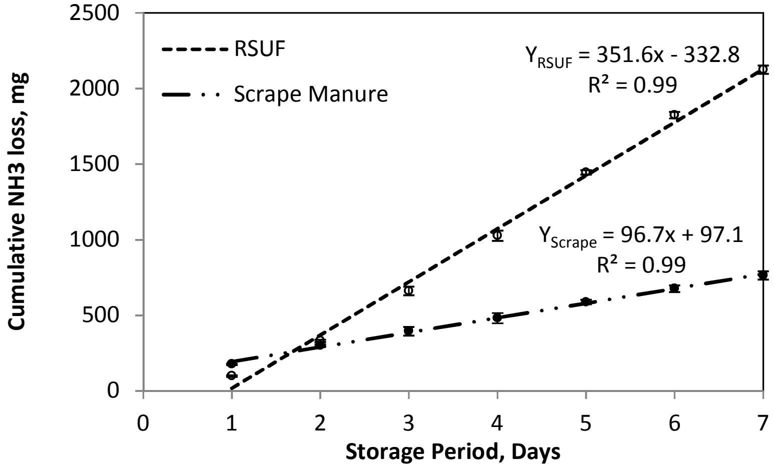

Figure 3.5. Ammonia emissions within the first week from aggregate of realistically separated urine and feces (RSUF) and from storage of conventional scrape manure (error bars indicate standard deviation from mean)

Details of cumulative NH_3 losses from storages of RSF and ISF within first two weeks are shown in Figure 3.6. It is clear that the rate of NH_3 losses from the storage of RSF is more than twenty times higher than that of the NH_3 losses from the storage of ISF, i.e. with no form of urine-feces contact at all. This clearly indicates that after the urine has been drained away from the feces, some of the urine would be entrapped in the feces. This entrapped urine would quickly be hydrolyzed by the urease enzyme present in the feces and subsequently released as NH_3. In addition, NH_3 release is pH dependent. Generally the pH of urine is around 9-10 implying that the pH of the feces would be increased by the entrapped urine; a factor that also could also increase NH_3 loss. The gradual NH_3 loss from the ISF may be attributed to the slow rate of breakdown of organic nitrogen by the heterotrophic bacteria.

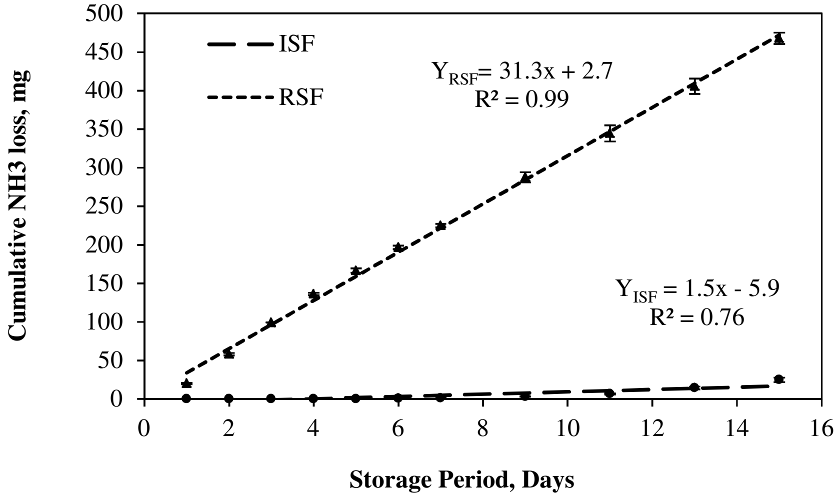

Figure 3.6. Ammonia losses from storages of realistically separated feces (RSF) and idealistically separated feces (ISF) within first two weeks (error bars indicate standard deviation from mean)

Profiles of short-term NH_3 losses from storages of RSU and ISU are shown in Figure 3.7. The rate of NH_3 loss from the RSU is more than twelve times greater than that from storage of the ISU in the first seven days. This is probably because the RSU has already been inoculated with urease enzyme upon the initial urine-feces contact. The urease enzyme present in the feces could have initiated hydrolysis of urinary urea into NH_3. In the first seven days of storage, the ISU had only marginally started losing some NH_3 (Figure 3.7). It appears that it would take at least 2-3 days for the urine to be inoculated with the critical mass of urease enzyme from the ambient environment to initiate urea hydrolysis.

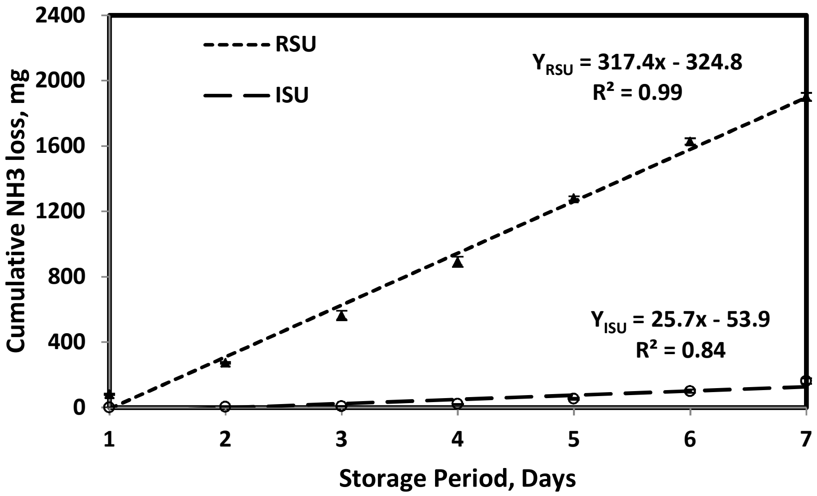

Figure 3.7. Ammonia losses from storages of realistically separated urine (RSU) and idealistically separated urine (ISU) within first week (error bars indicate standard deviation from mean)

Long term studies

A comparison of NH_3 emissions from the RSU and the ISU for the entire study-period is presented in Figures 3.8a & b. Ammonia losses from the RSU started right from the first day and continued throughout the first two weeks after which no further NH_3 loss was observed during the period of the study. The three replicate studies were fairly identical based on the standard deviations from the mean of the three replicates. On the other hand, NH_3 losses from two replicates of the ISU showed completely different trends. In view of this, NH_3 losses from two storages are presented in two ways: i) individually, i.e. not averaging the two replicates (Figure 3.8a), and ii) as one, i.e average of the two replicates (Figure 3.8b). The authors believe that the first replicate of ISU probably picked up the urease enzyme quicker than the second replicate because the enzymes in the environment are not evenly distributed. The earlier hydrolysis of urea in the first replicate explains the higher NH_3 loss within the three week period. Ammonia loss from the first replicate was almost over by the end of the 23-days period, while the second replicate was evidently still losing NH_3. In general, however, from these results we could infer that NH_3 loss from the storage of ISU will be potentially higher than the NH_3 loss from the storage of RSU. A possible explanation for the higher NH_3 loss from ISU was the absence of fecal solids material to bind NH_3 or impede the mass transfer mechanism of NH_3. Another possible explanation is the higher pH of ISU (10.0) over that of the RSU (9.7). In general, a higher pH increases the potential of NH_3 emissions.

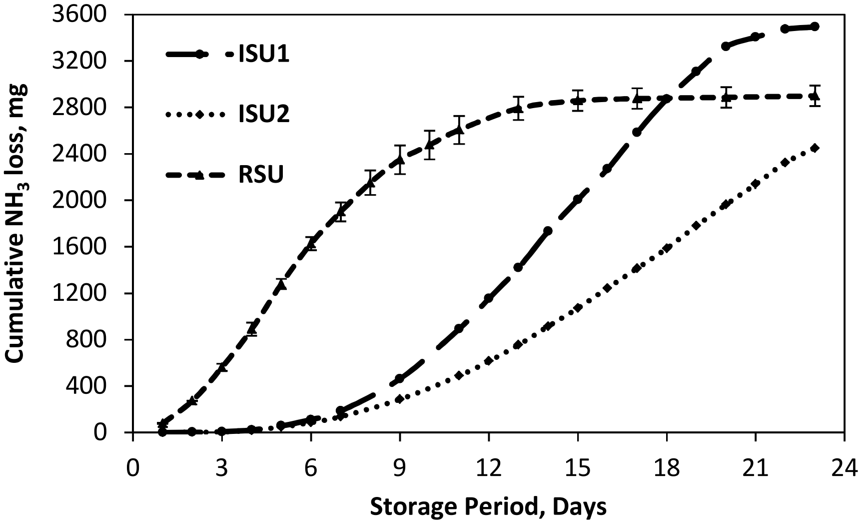

Figure 3.8a. Cumulative average (3-replicates) NH_3 losses from storages of realistically separated urine (RSU), and cumulative NH_3 losses from two replicates of idealistically separated urine (replicate-1 (ISU1) & replicate-2 (ISU2)) during entire study period (error bars indicate standard deviation from mean)

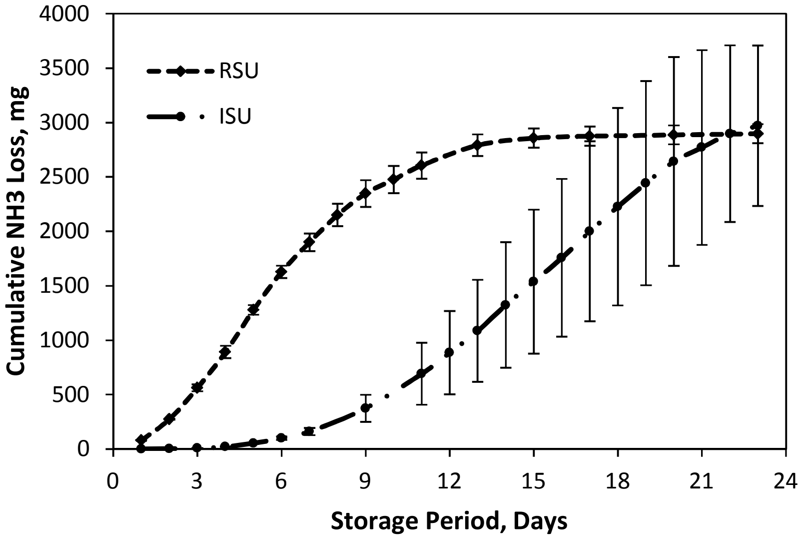

Figure 3.8b. Cumulative NH_3 losses from storages of realistically separated urine (RSU), and idealistically separated urine (ISU) during entire study period (error bars indicate standard deviation from mean)

The overall goal of this study was to determine if urine-feces separation can mitigate NH_3 emissions during post-separation storages of the separated urine and feces. This study examined NH_3 emissions from three scenarios: i) realistically separated urine and feces ii) Idealistically separated and feces and urine, and iii) scrape manure (as the control). The results of NH_3 emissions from storages of waste streams from these three scenarios are summarized in Figure 3.9. Given the same exposed surface areas for all storages, the combined emissions of the ISU and ISF from the post-separation storages during the first 3 weeks of storage would be the highest. However, from the observations, initiation of NH_3 loss would be delayed for about a week but will eventually exceed that from other storages. The NH_3 losses from the combined RSU and RSF were the next highest below that of the aggregate of the ISU and ISF storages. In general, NH_3 losses in descending order was: idealistically separated feces and urine, realistically separated urines and feces, and scrape manure storages. Based on these findings, it is apparent that the best strategy for mitigation of NH_3 losses from post-collection storages would certainly be manure scrapping. Although urine-feces separation mitigates NH_3 emissions in the barns (von Bernuth et al., 2005; Swierstra et al., 2001; Braam et al., 1997a, 1997b), the results from our studies indicate that separation of urine and feces could potentially exacerbate NH_3 emissions during post-separation storages.

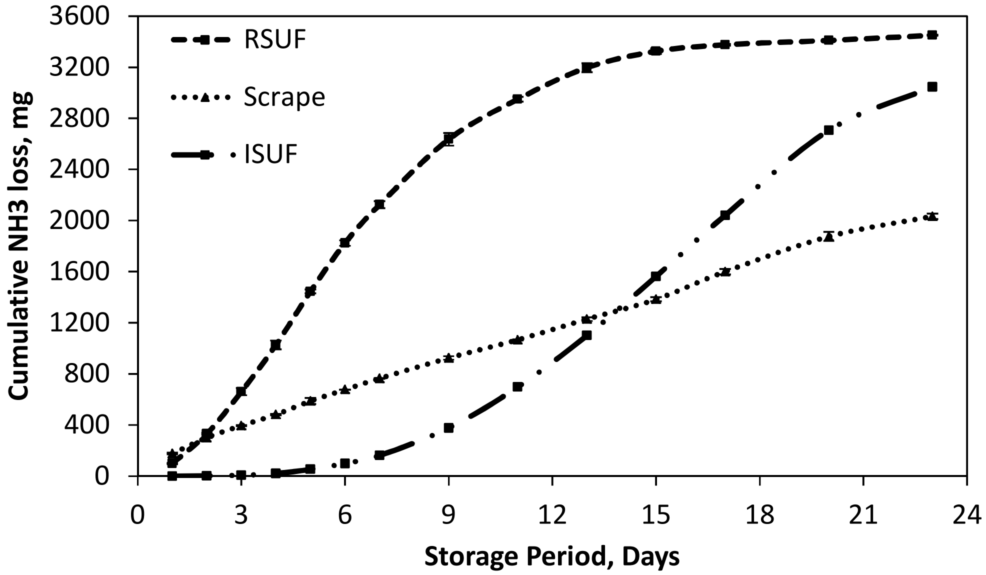

Figure 3.9. Ammonia emissions from aggregate of realistically separated urine-feces (RSUF), idealistically separated urine-feces (ISUF), and scrape manure storages during the prolonged study period (error bars indicate standard deviation from mean)

3.6 Summary and Conclusions

A series of laboratory scale simulation studies were conducted to evaluate NH_3 emission mitigation from post-collection storages of three waste streams: i) idealistically separated feces and urine (no contact between urine and feces), ii) realistically separated urine and feces, and iii) conventionally scraped manure. From the results of these studies, NH_3 emission from post-separation storage of realistically separated urine and feces within the first seven days was greater than that from the storages of the idealistically separated urine and feces. However, the idealistically separated urine eventually and rapidly lost NH_3 in the next two weeks resulting in higher NH_3 losses than that from storage of the realistically separated urine and feces by the end of the week 3.

Based on these studies, therefore, it is evident that avoiding the contact of urine and feces would not necessarily result in more reduction of NH_3 emissions. It appears that the effort of avoiding absolute contact of urine and feces will just delay the initiation of NH_3 loss by only a few days. This study indicates that the conventional method of scraping of urine and feces from barn would be a better strategy for reducing NH_3 emissions from post-collection storages compared to urine-feces separation approaches.

3.7 Acknowledgements

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CHAPTER FOUR

A Model for Overall Mass Transfer Coefficient of Ammonia from Dilute Dairy Manure Slurries

4.1 Abstract

Available data indicate that about 75-80% of total nitrogen entering a dairy operation is lost as ammonia (NH_3) from an anaerobic dairy lagoon and other similar manure storages. Direct measurement of NH_3 emissions from manure holding systems can be complicated and expensive, process-based emission models can be used to provide a cost effective alternative method for NH_3 emissions estimation. The overall mass transfer coefficient (K_{oL}) of NH_3 is an important component of any NH_3 emission process-based model. Models relying on purely theoretically derived K_{oL}s of NH_3 from livestock manures have not adequately predicted NH_3 emissions. In this study, the K_{oL} of NH_3 from dilute dairy manure slurries was modeled empirically, in a laboratory convective emission chamber (CEC), to determine realistic NH_3 K_{oL} values under typical conditions of the Pacific Northwest. The K_{oL} of NH_3 increased with both liquid temperature (T_L), and air velocity (V_{air}), but decreased with increase in both air temperature (T_{air}), and concentration of TS (total solids). The K_{oL}s of NH_3 ranged from 1.41×10^{-6} to 3.73×10^{-6} m/s. The obtained non-linear empirical model of K_{oL} of NH_3 from dilute dairy manure slurries had a coefficient of determination (R^2) of 0.83. This model is thus reliable for determining K_{oL} of NH_3 in ammonia emissions process-based models over the range of the experimental conditions considered in this study. The sensitivity of the K_{oL} of NH_3 to the four model parameters, in descending order was: T_L, V_{air}, T_{air}, and TS concentration, respectively.

Keywords: Overall mass transfer coefficient, K_{oL}, process-based models, convective emission chamber, dairy manure, lagoon, ammonia emissions.

4.2 Introduction

The largest source of global ammonia (NH_3) emissions is agriculture; with livestock production believed to contribute ~80% of the total agricultural emissions (De Visscher et al., 2002; Aneja et al., 2000; Kurvits and Marta, 1998; Sommer and Hutchings, 1995; Battye et al., 1994; Dentener and Curtzen, 1994). In addition, available data indicate that 75-80% of the total nitrogen (total-N) entering a dairy facility is lost from anaerobic lagoons via gaseous emissions (ICL and IDEAL, 2005). Even with more conservative estimates of 71% (EPA, 2002) and 50% (AEG USKH Inc., 2005) nitrogen loss into the air from anaerobic lagoons, it is clear that these are the major sources of NH_3 loss from dairy operations and are a concern because they not only pollute the environment, but also lower the fertilizer-value of the residual manure.

Determination of NH_3 emissions from agricultural facilities is critical to the control of environmental pollution as well as in regulating emissions from livestock operations. Direct NH_3 emissions measurement from such manure storage facilities is, however: challenging, extremely time consuming, and an expensive task (Liang et al., 2002). Since NH_3 emission is governed by both manure characteristics and meteorological conditions, this onerous task has to be performed for each separate livestock operation because no two operations will be similar in all respects. Process-based emission models offer an alternative approach for estimating NH_3 emissions from such systems, in a cost-effective manner, because process-based models generally only need determinations of key manure characteristics and meteorological conditions to predict NH_3 emissions from the system in question.

A generic process-based model for NH_3 emission from bulk liquid manure is presented in equation [1]: where Q_a = Ammonia flux g/s, K_{oL} = Overall convective mass transfer coefficient, m/s, A = Area of emitting surface, m^2, $[NH_3]_L$ = Ammonia concentration at the lagoon liquid surface, g/m^3, and $[NH_3]_a$ = Ammonia concentration in air, g/m^3 (Ni, 1999).

$$Q_a = K_{oL} A([NH_3]_L - [NH_3]_a) \qquad [1]$$

Two key parameters required as inputs in equation [1] are the overall mass transfer coefficient (K_{oL}) of NH_3, and the dissociation constant (K_d) of ammonium ion (NH_4^+). The K_{oL} of NH_3 is the desorption rate of free NH_3 from liquid surface into the free air stream, while the K_d of NH_4^+ determines the fraction of the volatile NH_3 in the total ammonical nitrogen (TAN) in the bulk liquid. The K_{oL} of NH_3 from liquid manure depends on several factors including the: TAN concentration in the liquid, liquid pH and temperature, ambient air temperature, solids concentration, and wind speed (De Visscher et al., 2002; Arogo et al., 1999; Ni, 1999). Arogo et al.'s (1999) modeled K_{oL} of NH_3 from an anaerobic under floor swine manure pit using data from a series of laboratory experiments conducted in a convective emissions chamber (CEC). The latter studies showed that the K_{oL} of NH_3 depended on all the three factors that were considered, namely: air flow velocity (V_{air}), lagoon-liquid temperature (T_L), and air temperature (T_{air}). Their model did not consider the contribution of the solids on the K_{oL} of NH_3, which other researchers have indicated is significant (De Visscher et al., 2002; Zhang et al., 1994).

Ni (1999) reported empirical values of the K_{oL} of NH_3 from livestock manure in a review paper and most of the reported values were for swine lagoon wastewaters, no values were reported for dairy wastewaters. Rumburg et al., (2008b) in a more recent study compared direct measurements of NH_3 emissions with predictions of a process-based model using theoretical and empirical values reported from Ni (1999) of the K_{oL} of NH_3 in dairy manures. Rumburg et al. (2008b) results indicated significantly wider errors with the theoretically derived K_{oL} values (120% normalized mean error (NME) compared with empirical values (21% NME). Because theoretical derivations of K_{oL} of NH_3 from livestock wastewaters are inadequate and no empirical K_{oL}s of NH_3 are available for dairy wastewaters (Ni. 1999), an empirical model of the K_{oL} of NH_3 from dairy wastewater is critical to further improvement of NH_3 emissions models. The overall objective of this research was to develop an empirical sub-model of K_{oL} of NH_3 from liquid dairy wastewater to improve the reliability of NH_3 emission process-based models.

4.3 Materials and methods

Theory behind determination of K_{oL}

Ammonia release from an anaerobic dairy lagoon wastewater depends on the resistance of its transfer, and the concentration gradient between the lagoon liquid and the atmosphere (Arogo et al. 1999) (Equation [1]). A conceptual process of NH_3 release from an anaerobic dairy lagoon is given in the Figure 4.1.

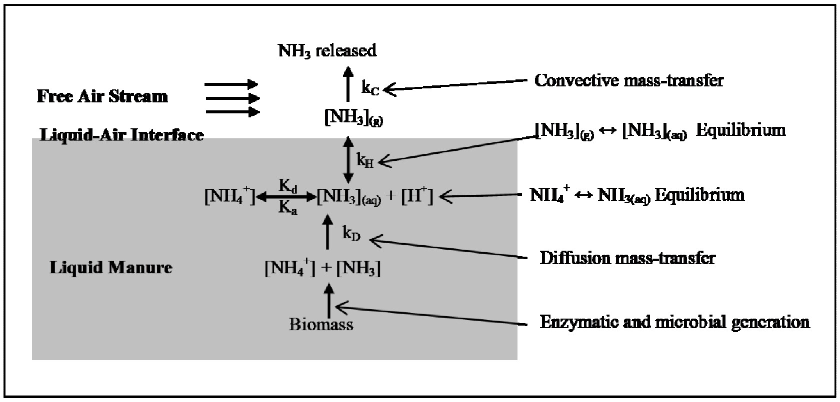

Figure 4.1. Ammonia release mechanism from liquid manure (Ni, 1999)

From Figure 4.1, it is clear that NH_3 emission from the bulk manure liquid into the atmosphere is influenced by the Henry's constant (k_H) and convective mass transfer (k_C) in gaseous phase. The K_{oL} of NH_3 presented in Equation [1] is a function of k_H and convective mass transfer coefficient. In comparison to K_{oL}, however, the effect of diffusion mass transfer is negligible and is usually omitted in most process models. In addition, NH_3 concentration in air is also negligible compared with its concentration in the liquid, especially for open-surface storages. Equation [1] can thus be re-written as equation [2], where *t* is the time step and the negative sign indicates that NH_3 concentration decreases with time. Equation [2] can further be simplified to Equation [3] by noting that $M_{TAN} = V \times TAN$, where V=volume of manure.

$$\frac{dM_{TAN}}{dt} = -K_{oL} A [NH_3]_L \qquad [2]$$

$$\frac{dTAN}{dt} = -K_{oL} \frac{A}{V} [NH_3]_L \qquad [3]$$

Equation [3], however, cannot be used to compute K_{oL} because it is impossible to measure the concentration of NH_3 (i.e. $[NH_3]_L$ in this equation) in the wastewater. Substituting $\alpha \times TAN$ for $[NH_3]_L$ in the Equation [3] and integrating translates into Equation [4]; where, "α" is the unionized (NH_3) fraction of TAN in the liquid manure, and $TAN_{0,L}$, and TAN_t are the initial and current concentrations of TAN in the bulk manure liquid at a given time t, respectively. At liquid pHs above 11.0 all the TAN is in the form of free NH_3 and α=1 (see Figure 4.2). The logarithmic form of Equation [4] given in Equation [5] is more preferable form because for α =1 and known A, and V, K_{oL} is computable from the slope of linear regression plot.

$$TAN_t = TAN_{0,L} \times e^{-(K_{oL}\alpha\frac{A}{V})t} \qquad [4]$$

$$\ln\left(\frac{TAN_t}{TAN_{0,L}}\right) = -K_{oL}\alpha\frac{A}{V}t \qquad [5]$$

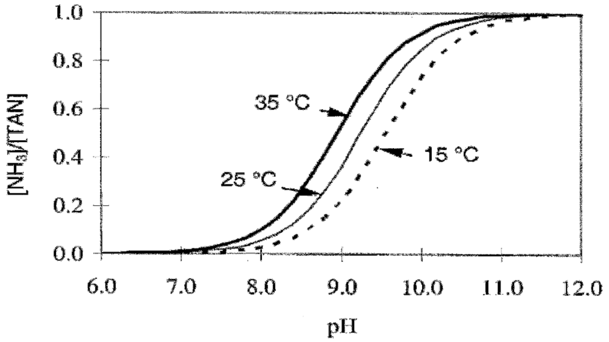

Figure 4.2. Function of NH_3/NH_4^+- equilibrium with temperature and pH in aqueous solutions (Loehr, 1974)

Instrumentation

The dimensions and layout of the test section of the convective emissions chamber (CEC) are shown in Figure 4.3, and a photograph of the CEC is shown in Figure 4.4. The CEC was similar to those of previous studies (Arogo et al. 1999, Shaw, 1994, Zhang, 1992). The CEC consisted of a blower, a flow-controller unit, screens to create turbulence, and a sample-chamber. The overall dimensions of the CEC were 4.2m × 0.45m × 0.15m (L × W × H). The test section dimensions of the CEC were 1.2m × 0.45m × 0.15m (L × W × H) and the CEC-walls were insulated. Two thermocouples as pictured were used to control the T_{air} within ±1°C. The V_{air} was controlled using a damper at the inlet of the air generator within ±0.1 m/s. The sample test-pan with dimensions 27.9cm × 17.8cm × 3.5cm (L × W × H) was placed in a constant temperature water bath to maintain set temperatures during the experiments. The water bath maintained specified temperatures within a range of 0–100°C.

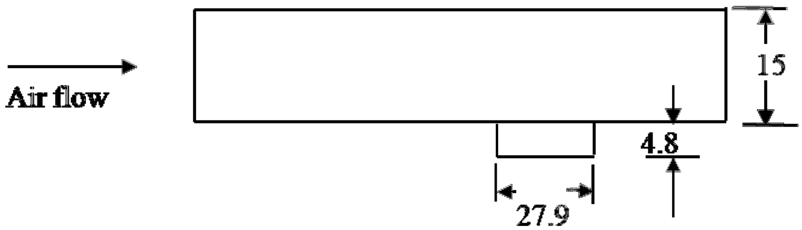

Figure 4.3. A cross-section view of the convective emission chamber test-section (all dimensions in cm but not to scale)

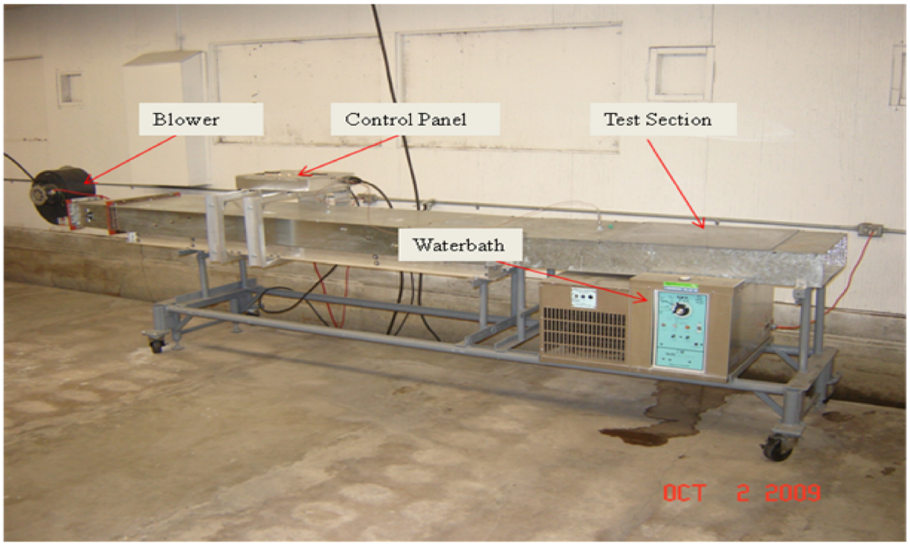

Figure 4.4. A full-size photograph of the Convective Emission Chamber (CEC) Lab

Experimental Design

The K_{oL}s of NH_3 were determined under the following randomized conditions:

1. Air temperatures: 15, 25, and 35°C;
2. Air velocities: 0.5, 1.0, 1.5, 2.5, and 4.0 m/s;
3. Manure liquid temperatures: 5, 15, 25 and 35°C; and
4. Concentrations of TS: 0.5, 1.0, 1.5, 2.0, 2.5% (w/w basis); which is the typical range of TS for dairy lagoon liquid.

Dairy manure (with concentration of TS of ~3.0% and 500 mg/L TAN) was obtained from Washington State University Knott Dairy Research Center, Pullman, WA. The manure preparation consisted of dilution to the desired TS concentrations followed by pH adjustments to the desired levels. Dilutions were made with tap water to desired TS concentrations ranging from 0.5 to 2.5%. The pH was adjusted to 12.0, using 10M NaOH, to ensure that all TAN was in the form of free NH_3 (or $\alpha=1$: according to Figure 4.2). The prepared manure sample was poured into the test pan, placed in the water-bath, and allowed to attain the specified liquid-temperature. The temperature of the manure sample was checked frequently with a thermometer to ensure constant temperature conditions were maintained.

The CEC was run for another 30 minutes to allow the manure sample to stabilize to the test conditions. Once the manure attained test conditions, 1 mL samples were drawn 2 mm below liquid surface at 5 locations in the test pan every 30 minutes for 4 hours. To minimize further NH_3 loss, 5mL of 2M sulfuric acid was added to each collected sample. The samples were analyzed immediately after the experiment using standard methods (APHA 1992). Each test-condition was replicated 3 times.

The test-conditions (Table 4.1) represent the expected ranges of the characteristics of dilute manure in anaerobic dairy lagoons (and other similar storages), and environmental conditions encountered in the US Pacific Northwest.

Table 4.1. Experimental plan for the determination of overall mass transfer coefficient of ammonia in liquid-dairy manure

Run #	Air Temperature °C	Air Velocity m/s	Liquid Temperature °C	Solids Content % W/W
1	25	0.5	25	1.5
2	25	1	25	1.5
3	25	1.5	25	1.5
4	25	2.5	25	1.5
5	25	4	25	1.5
6	25	1.5	5	1.5
7	25	1.5	15	1.5
8	25	1.5	35	1.5
9	25	1.5	25	0.5
10	25	1.5	25	1.0
11	25	1.5	25	2.0
12	25	1.5	25	2.5
13	15	1.5	25	1.5
14	35	1.5	25	1.5

4.4 Model development and data analysis

Model Development

Several modeling approaches for the K_{oL} of NH_3 from livestock wastewaters and from pure waters are documented in literature (Liu et al., 2008; Liu et al., 2007; Arogo et al., 1999; Guo and Roache, 2002; Hasalm et al., 1924). Arogo et al. (2003); Guo and Roache (2002), modeled K_{oL} of NH_3, and K_{oL} in six different organic compounds in laboratory convective emission chambers using the Sherwood number (dimensionless) approach as illustrated in equations [6], [7], [8], and [9]: where S_h = Sherwood number, also represented as Equation [7]; R_e, and S_c are Reynolds (Equation [8]), and Schmidt [9]) numbers respectively; C_{KoL} is a constant of K_{oL}, and *a,* and *b* are exponents; and K_{oL} is the overall mass transfer coefficient; L is characteristic length; $D_{A\text{-}air}$ is NH_3 diffusivity in air; ρ_{air} is density of air; V_{air} is air velocity; and μ_{air} is coefficient of dynamic viscosity of air. Hasalm et al. (1924) developed a mass transfer coefficient model of NH_3 in pure water taking two factors, $V_{air,}$ and T_L, into consideration. Arogo et al., (1999) in their study determined that the K_{oL} of NH_3 in swine manure was directly proportional to V_{air}, T_L and inversely proportional to T_{air}.

$$S_h = C_{KoL}(R_e)^a(S_c)^b \qquad [6]$$

$$S_h = \frac{K_{oL}L}{D_{A-air}} \qquad [7]$$

$$R_e = \frac{\rho_{air}V_{air}L}{\mu_{air}} \qquad [8]$$

$$S_c = \frac{\mu_{air}}{\rho_{air}D_{A-air}} \qquad [9]$$

In this study, empirical K_{oL}s of NH_3 obtained from a series of studies conducted in CEC were considered as the basis for formulating an equation for the K_{oL} of NH_3 from dairy manure slurries. First, Equation [10] was formulated considering all the factors included in obtaining the empirical K_{oL}s of NH_3. Second, Equations [11] and [12] were then formulated by noting that the: (i) K_{oL}s of NH_3 increased with increase in V_{air} and T_L, and (ii) K_{oL}s of NH_3 decreased with increases in T_{air} and concentration of TS: where: C_{KoL} is a constant of proportionality; and *a, b, c,* and *d* the respective exponents.

$$K_{OL} = f\{T_L, T_{air}, V_{air}, TS\} \qquad [10]$$

So, $$K_{OL} \propto \frac{(T_L)^a (V_{air})^b}{(TS)^c (T_{air})^d} \qquad [11]$$

$$K_{OL} = C_{K_{OL}} \frac{(T_L)^a (V_{air})^b}{(TS)^c (T_{air})^d} \qquad [12]$$

Data analysis

The constants *C_{KoL}, a, b, c,* and *d* in equation [12] were obtained using Proc NLIN SAS (SAS Institute Inc, 2006) and the empirical K_{oL}s of NH_3 data obtained from a series of experiments conducted in the CEC. SAS was also used to conduct analysis of variance (ANOVA) to determine factors that significantly influence determination of K_{oL} of NH_3. All tests were performed at a significant level of $\alpha = 0.05$.

4.5 Results and discussions

Computations of K_{oL}s of NH_3

The exponential decay of TAN concentration in the liquid dairy manure test sample from the start to the end (240 minutes) of a typical test run conducted at T_L=25°C, T_{air}=25°C, V_{air}=1.5m/s, TS=1.5%, and at a pH of 12 is shown in the Figure 4.5. The TAN concentration residual curve evidently followed first order reaction kinetics as indicated by a strong correlation of determination (R^2) of 0.96. Based on the slope of the linear regression plot in Figure 4.5 and Equation [5], the computed K_{oL} of NH_3 was 2.1×10^{-06} m/s. This procedure of computing the K_{oL}s of NH_3 was repeated for all the other test-conditions examined in this study to generate K_{oL}s data for modeling K_{oL} of NH_3 in dairy manure within the test-conditions.

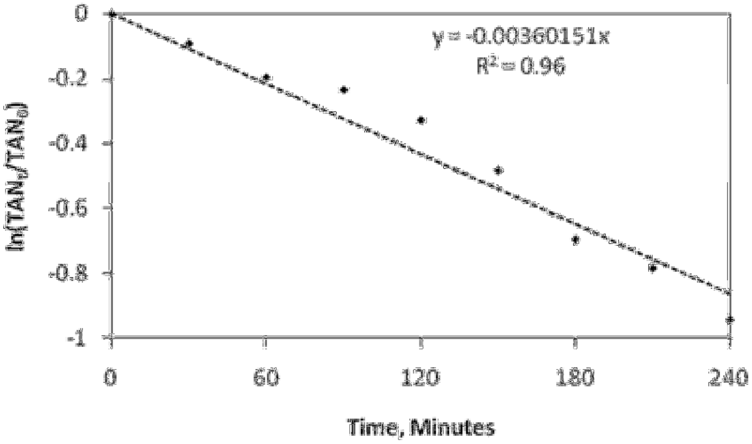

Figure 4.5. TAN decay residuals curve for dairy manure at T_L=25°C, T_{air}=25°C, V_{air}=1.5m/s, TS=1.5%, and pH 12

In general, the TAN decay curves in the liquid dairy manure samples for constant concentrations of TS, T_{air}, and V_{air} at liquid manure temperatures (T_L) of 5, 15, 25 and 35°C were similar and followed the trend shown in Figure 4.6. All the decay curves of the concentration of TAN similarly followed first order reaction rates with strong coefficients of determination (R^2, ranging from 0.95 to 0.99). The general trend was the increase in the K_{oL} with increase in liquid manure temperature. A similar trend was reported by Arogo et al. (1999) for K_{oL} of NH_3 in swine manure. In a review paper Ni (1999) the reported K_{oL}s of NH_3, aggregated from multiple studies for swine manure, ranging from $1.3x10^{-06}$ to $11.7x10^{-03}$ m/s. The results obtained from this study ($1.41x10^{-06}$ to $3.73x10^{-06}$ m/s) were also within this broad range.

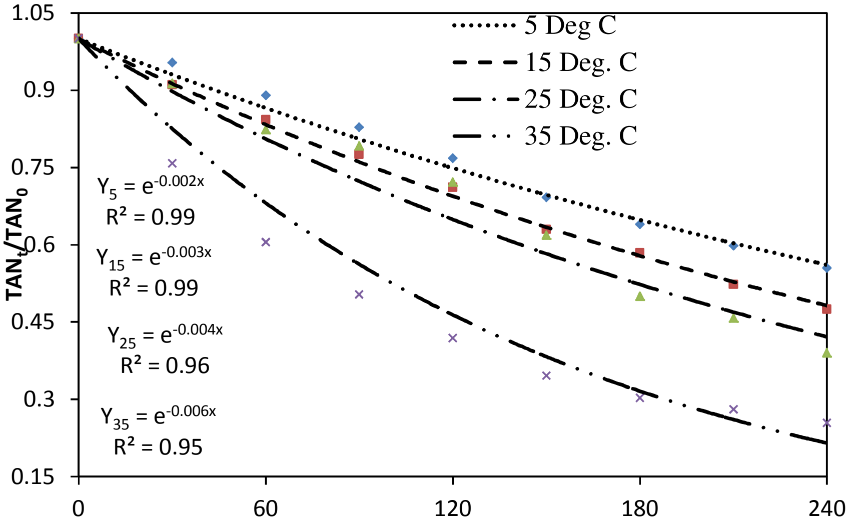

Figure 4.6. Ammonia decay curves over a period of 4 hours at 12 pH, air velocity 1.5 m/s, TS concentrations 1.5%, and at liquid temperature 25°C

Effect of Liquid Temperature (T_L) on K_{oL} of NH_3

The K_{oL}s of NH_3 in liquid dairy manure at four liquid temperatures examined in this study are given in Table 4.2, while the exponential regression analysis showing the effect of T_L on K_{oL} of NH_3 is presented in Figure 4.7. In theory, the viscosity of liquids decreases with increase in temperature. As the liquid manure temperature increases, the K_d of NH_4^+ increases. With lower liquid viscosity, the resistance for the release of free NH_3 decreases in the bulk of the liquid and therefore, NH_3 releases quickly out of the liquid. This phenomenon was evident from the experimental results obtained in this study. In general, the K_{oL} of NH_3 increased linearly with increase in the liquid temperature. Similar trends were observed in the K_{oL} of NH_3 in swine manure in earlier studies (Arogo et al., (1999). In summary: as liquid temperature increases the free NH_3 fraction increases linearly and consequently the potential of NH_3 emission into the environment. Ammonia emissions from the anaerobic dairy lagoons and other similar facilities are thus higher in warm seasons (and during the day) and lower in colder seasons (and at night).

Table 4.2. K_{oL} values obtained for four liquid temperatures

Liquid Temperature °C	K_{oL} values × 10^{-6} m/s
5	1.41±0.02
15	1.77±0.08
25	2.13±0.23
35	3.73±0.04

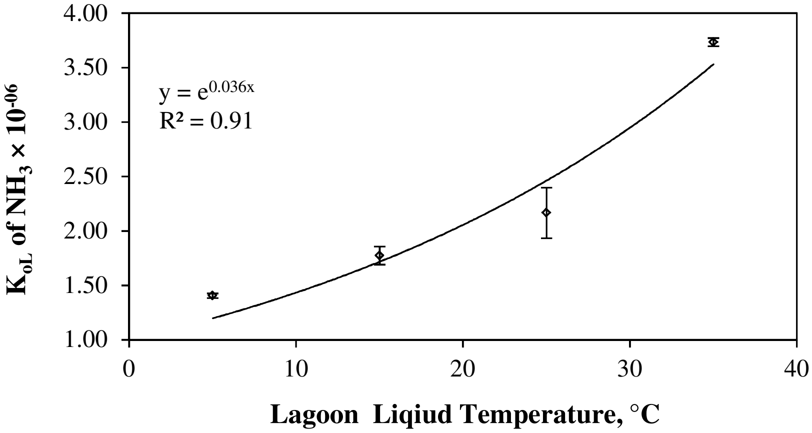

Figure 4.7. K_{oL} of NH_3 as a function of liquid temperature (T_L) (error bars indicate standard deviation from mean)

Effect of Air Velocity (V_{air}) on K_{oL} of NH_3

The K_{oL} of NH_3 as a function of air velocity (V_{air}) at T_{air} of 25°C, T_L of 25°C, and concentration of TS of 1.5% is shown in Figure 4.8. Based on the strong (R^2=0.92) linear regression plot, we infer that the K_{oL} of NH_3 in liquid dairy manure is directly proportional to the air velocity above the liquid-air interface. This relationship is consistent with the theoretical expectation because higher wind velocities result in faster removal of NH_3 from the air above the liquid-air interface. Removal of NH_3 from the air above the liquid-air interface reduces NH_3 partial pressure leading to its enhanced volatilization. Storage of manure in locations that experience the strongest winds, therefore, results in the highest NH_3

release. In general, this scenario results in lower NH_3 concentration $[NH_3]_a$ term in the Equation[1] and hence higher concentration difference; which all translates into more NH_3 loss. A similar trend was also observed in previous studies with swine manure (Arogo et al., 1999).

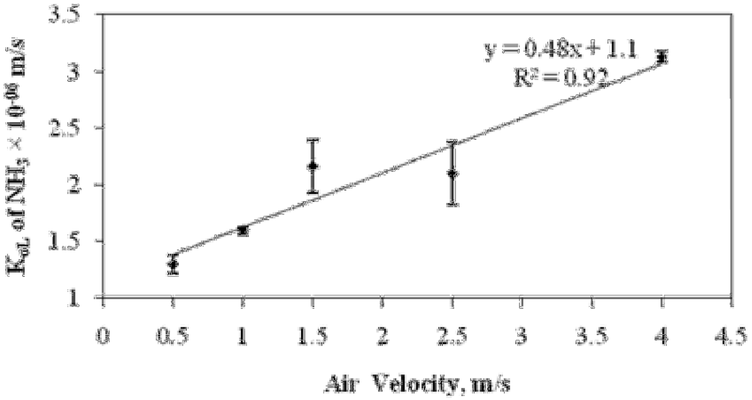

Figure 4.8. Relationship between K_{oL} of NH_3 and air velocity (error bars indicate standard deviation from mean)

Effect of Air Temperature, T_{air}, on K_{oL} of NH_3

In general, when the temperature of an ideal gas (air in this case) increases, its coefficient of dynamic viscosity (μ) increases. This phenomenon in turn increases resistance to volatilization from the emitting surface. The relationship between the K_{oL} of NH_3 and air temperature is shown in Figure 4.9. The strong linear regression graph, indicated by the high correlation of determination (R^2) of 0.99, suggests that K_{oL} of NH_3 decreases with increase in air temperature. Increase in viscosity of ambient air with temperature increases the resistance to the NH_3 volatilization, which is reflected in decreased K_{oL} of NH_3 from the liquid manure. Based on these results, locations with higher air temperatures offer more resistance to NH_3 air pollution. When the ambient air temperatures are high, however, the liquid temperatures are also high. In this case, whichever of these two temperatures dominates determines whether NH_3 release to the surrounding air will occur or not. Results of this study indicate a 1.4-fold increase in the K_{oL} of NH_3 for every 10°C rise in T_L, and 1.2-fold decrease for every 10 degree rise in T_{air}. Therefore, if both T_L and T_{air} increase by a margin of 10°C, the effect of T_L would be relatively higher; leading to net NH_3 loss.

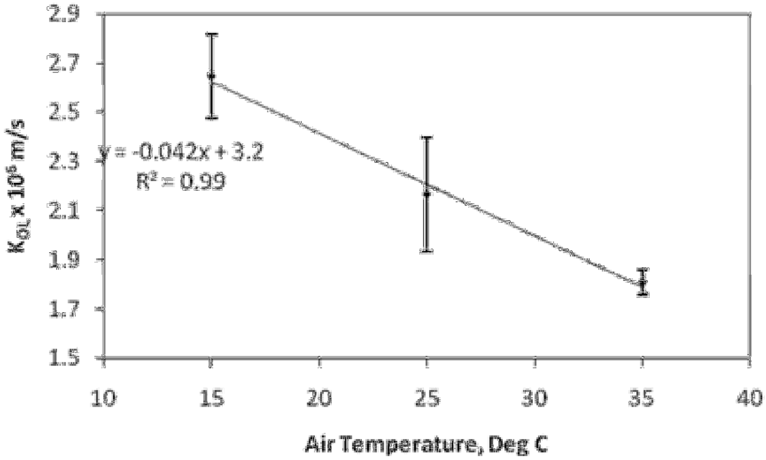

Figure 4.9. K_{oL} of NH_3 as a function of Air Temperature (error bars indicate standard deviation from mean)

Effect of Concentrations of TS on K_{oL} of NH_3

The effect of the concentration of TS on the K_{oL} of NH3 in dairy manure is presented in Figure 4.10. The linear regression plot has good correlation coefficient with an R^2 value of 0.78. The K_{oL} of NH_3 in the liquid dairy manure decreased with increase in the concentration of TS. In previous research, Arogo et al. (1999) observed no significant effect of the TS concentration on the K_{oL} of NH_3 from liquid swine manure when the TS concentration was lower than 1.0%. In this study, however, significant differences in the K_{oL}s of NH_3 at TS concentration of 0.5 and 1.0% were observed. In general, however, the K_{oL} of NH_3 decreased with increase in the TS concentrations: from $3.25x10^{-06}$ to $2.02x10^{-06}$ m/s at the TS concentration of 0.5 and 2.5 %, respectively. Apparently, solids inhibit NH_3 loss from dairy liquid manure: and the more the TS the more the inhibition as suggested by De Visscher et al. 2002.

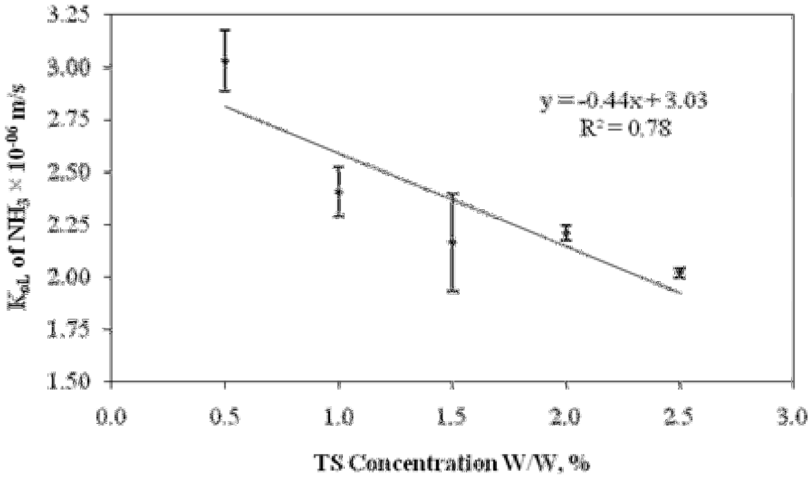

Figure 4.10. Effect of total solids on K_{oL} (error bars indicate standard deviation from mean)

Model Development

Linear regression analyses were performed to determine the effect of T_L on the K_{oL}s of NH_3 at 5, 15, 25, and 35°C (Figure 4.7), effect of V_{air} on the K_{oL} of NH_3 at 0.5, 1.0, 1.5, 2.5, and 4.0 m/s (Figure 4.8), and effect of T_{air} on the K_{oL} of NH_3 at 15, 25, 35°C (Figure 4.9). Further, non-linear regression analysis was performed to analyze effect of TS concentration on K_{oL} of NH_3 at 0.5, 1.0, 1.5, 2.0, and 2.5% W/W (Figure 4.10). These regression analyses were performed in order to formulate Equation [12].

The NH_3 K_{oL}s for dairy manure obtained from this laboratory study were combined with a non-linear regression model (Equation 12), and coded in Proc NLIN SAS (SAS Institute Inc, 2006) to obtain the values of constants a, b, c, d, and C_{KoL}. Equation [13] is the resulting empirical model of the K_{oL} of NH_3 in dairy manure liquid within the ranges of dairy manure characteristics and environmental conditions considered in this study. The strong coefficient of determination (R^2) of 0.83 of this model indicates good consistency with the experimental data. This model is thus reliable for determining the K_{oL} of NH_3 from liquid dairy manure slurries with the manure characteristic and environmental conditions covered in this study.

$$K_{oL} = 4.85\times10^{-11}\,\frac{(T_L)^{9.7}(V_{air})^{0.34}}{(T_{air})^{8.02}(TS)^{0.26}} \qquad [13]$$

Model Verification

A plot showing comparison between the measured K_{oL}s of NH_3 and model predicted K_{oL}s of NH_3 (from Equation [13]) from liquid dairy manure is presented in Figure 4.11. The results indicate good agreement between the measured and the predicted K_{oL}s of NH_3 with an NME of 9.6%. The normalized mean error (NME) is calculated using equation [14]: where n is the number of data values, X_{mod} and X_{mea} are the modeled and measured K_{oL}, respectively.

$$NME = \frac{\sum_{1}^{n}\left|X_{mod} - X_{mea}\right|}{\sum_{1}^{n} X_{mea}}\times100\% \qquad [14]$$

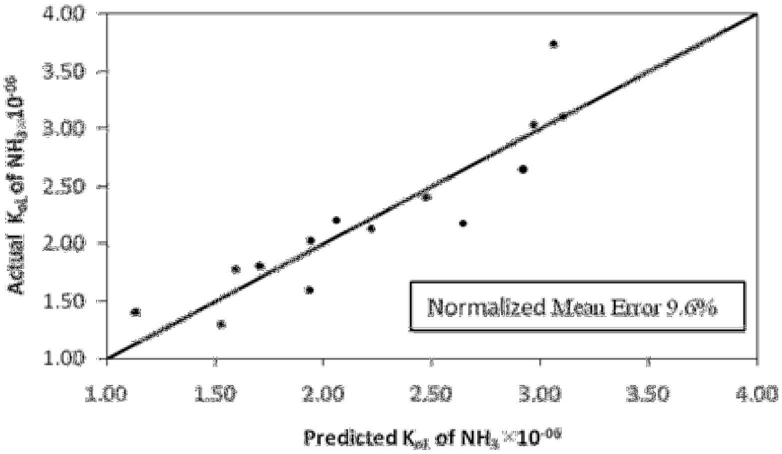

Figure 4.11. Comparison of the actual and the predicted K_{oL}s of NH_3 values in dairy manure slurries

Sensitivity Analysis

The model parameters that affect the K_{oL} of NH_3 for dilute dairy manure slurries are: T_{air}, V_{air}, T_L, and TS concentrations. Therefore, a sensitivity analysis was performed to evaluate the sensitivity of model predictions for K_{oL} of NH_3 (Equation [13]) by varying these factors and results are presented in Tables 4.3 and 4.4. These analyses were performed in two ways. First, the overall sensitivity of the model was evaluated by varying all model parameters simultaneously from the middle of each parameter's range (i.e. the midpoint) to lowest and highest points in the respective range (Table 4.3). Second, the model sensitivity was evaluated by varying individual model parameter one at a time from the midpoint to lowest and highest points in their respective parameter's range; holding all other parameters constant (Table 4.4). When all model parameters were simultaneously decreased from their respective midpoints to lowest possible levels, the model sensitivity was decreased by 37.0%. The model sensitivity was increased by 32.6% when all model parameters were increased simultaneously from their respective midpoints to highest possible levels.

Table 4.3. Overall sensitivity analysis of the model predicted K_{oL} of NH_3

Parameter/ Range	**T_L, °C**	**TS %**	**V_{air}, m/s**	**T_{air}, °C**	**Predicted KoL of NH_3, m/s × 10^{-06}**	**Sensitivity, %**
Below Midpoint	5	0.5	0.5	15	1.46	-37.0
Above Midpoint	35	2.5	4.0	35	3.08	32.6

T_L = Lagoon-liquid temperature; T_{air} = Air temperature; V_{air} = Air velocity; TS = Total solids concentration w/w

The effect of each model parameter on the sensitivity of K_{oL} of NH_3 model is presented in Table 4.4. The results of sensitivity analysis showed that the model is sensitive in descending order to: T_L, V_{air}, T_{air}, and TS concentrations respectively. Results show that the model for K_{oL} of NH_3 is greatly sensitive to the T_L. The sensitivity of the model with respect to T_L was greater above the midpoint (62.0%) than below the midpoint (-40.0%). It is evident that the K_{oL} of NH_3 will be more in the regions having warm T_Ls than the regions with cold T_Ls. The K_{oL} was more sensitive to V_{air} at the lower V_{air} (-40.0%) range than at the higher range of V_{air} (22.0%). The model of K_{oL} of NH_3 was more sensitive at the lower range of T_{air} (31.0%) than at the higher range of T_{air} (-23.0%); and more sensitive at lower TS content (33.0%) than at higher TS content (-12.0%).

Table 4.4. Sensitivity analysis of the effect of each model parameter on the K_{oL} of NH_3

Parameter	Point in the Range		K_{oL} m/s (10^{-06})	Sensitivity %
T_L, °C	5	L	1.34	-40.0
	20	M	2.32	--
	35	H	3.62	62.0
V_{air}, m/s	0.5	L	1.39	-40.0
	2.25	M	2.32	--
	4.0	H	2.82	22.0
T_{air}, °C	15	L	2.93	31.0
	25	M	2.32	--
	35	H	1.71	-23.0
TS Content, %	0.5	L	2.93	33.0
	1.5	M	2.32	--
	2.5	H	1.95	-12.0

L = Lowest; M = Midpoint; H= Highest

4.6 Summary and conclusions

The overall mass transfer coefficient of NH_3 from bulk liquid dairy manure to air was statistically modeled using data from a series of experiments performed in a laboratory convective emission chamber. The followings conclusions were drawn from results of those experiments and associated modeling process:

1. The K_{oL} of NH_3 increased with increase in T_L between 5 and 35°C. An increase in the liquid manure temperature, therefore, increases NH_3 emission into the environment.
2. The K_{oL} increased with increase in V_{air} within the range examined in this study (0.5 to 4.0 m/s); which implies NH_3 loss increases with increasing V_{air}.
3. The K_{oL} of NH_3 decreased with increase in T_{air} within 15-35°C range. Since ambient V_{air} and T_L move in the same direction, these two parameters counteract the effect of each other. The increase in NH_3 loss due to increasing T_L is moderated by decrease in NH_3 loss attributed to the simultaneous increasing ambient T_{air}.
4. The K_{oL} of NH_3 decreased with increase in the concentrations of TS in the range of 0.5 to 2.5%; suggesting that solids inhibit the mass transfer coefficient of NH_3 from liquid dairy manure. The higher the concentration of TS, the higher the inhibition and the lower the NH_3 loss.
5. The developed model for predicting the K_{oL} of NH_3 from liquid dairy manure exhibited an NME of 9.6%; demonstrating good fit with the experimental data.
6. The sensitivity of K_{oL} of NH_3 to all four model parameters was observed to be as followed, in descending order: T_L, V_{air}, T_{air}, and TS concentrations, respectively.
7. The model was more sensitive in the range above midpoint than in the range below midpoint when all the model parameters were simultaneously varied from midpoint to each way.
8. Each model parameter one at a time was varied from its midpoint to lowest and highest points in the respective parameter's range holding all other parameters constant. The model sensitivity was: greater above the midpoint than below the midpoint with in T_L range; greater below the midpoint than above the midpoint for the V_{air} range; higher below the midpoint than above the midpoint of the T_{air} range; and for TS content range, more below the midpoint than above the midpoint.

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CHAPTER FIVE

A Model of Ammonium Ion Dissociation in Liquid Dairy Manure

5.1 Abstract:

Emission of Ammonia (NH_3) from lagoons and other similar structures holding liquid dairy manures contributes to environmental pollution and also lowers the fertilizer-value of the liquid-effluent. In general, NH_3 volatilization from these facilities depends on the concentration of free NH_3 in the liquid, which is a function of the dissociation of ammonium ion (NH_4^+). The dissociation of NH_4^+, on the other hand, is dependent on the: liquid temperature, liquid pH, and concentration of total solids (TS). In this study ammonium ion (NH_4^+) dissociation constant (K_d) was empirically modeled at a pH of 9; at four temperatures (5, 15, 25, and 35°C), generally experienced in the US Pacific Northwest, and five TS concentrations (0.5, 1.0, 1.5, 2.0, and 2.5%; w/w) common in flushed-dairy manure. The K_d of NH_3 increased 1.61 times for every 10 °C rise in temperature. The data also indicated a linear decrease in the K_d of NH_4^+ with increase in the concentration of TS in the liquid. The resulting empirical model of the K_d of NH_4^+ as a function of temperature and TS had a coefficient of determination, R^2, of 0.97; demonstrating a good fit to the experimental data. The K_ds of NH_4^+ in the dairy manure liquid were 117%, 87%, 61%t, and 54% compared to the theoretical K_ds of NH_4^+ in pure water at 5, 15, 25, and 35°C, respectively. The results of this study emphasize the need for: (i) including both the liquid-TS and the liquid-temperature in models of K_d of NH_4^+ in livestock wastewaters, and (ii) covering the entire ranges, of both parameters, encountered in the region where the model will be used.

Keywords: Ammonium dissociation constant, liquid-dairy manure, modeling, connective emission chamber (CEC), ammonia emission, ammonia volatilization.

5.2 Introduction

In liquid dairy-manure, nitrogen (N) exists both in inorganic and organic forms. Total ammonical nitrogen (TAN) which is inorganic in nature is the sum of ammonium ion (NH_4^+) and unionized ammonia (NH_3) forms of N. In general, only the latter (NH_3-N) nitrogen species volatilizes from dairy wastewater into the atmosphere. Therefore, presence of NH_3 in the manure increases the potential of air pollution from the animal feed operations (Sommer et al., 2005; Ni, 1999). In addition to potential air pollution, emission of NH_3 also reduces the fertilizer value of the dairy-lagoon effluents when it is eventually applied on crop-fields or pastures (Sørensen and Amato, 2002).

In general, there are no direct methods for estimating the proportion of NH_3 in the TAN in aqueous solutions. However, several methods exist to analyze the TAN concentration in aqueous solutions (APHA 1998). In aqueous solutions, unionized NH_3 and hydrogen ion (H^+) exist in equilibrium with NH_4^+ as presented in Equation [1] (Sommer et al., 2005), which will generally depend on the solution temperature and pH. Lowering the liquid pH shifts the equilibrium to the right thus lowering the concentration of NH_3 in the liquid. This is basic theory behind acidification of manure slurries to mitigate emissions of NH_3 or to prevent loss of NH_3 during storage of manure samples.

$$\left[NH_4^+\right] \leftrightarrow \left[NH_3\right] + \left[H^+\right] \qquad [1]$$

A mathematical expression for NH_4^+ dissociation constant (K_d) which is good for dilute aqueous solutions only (Arogo et al. 2002), and the corresponding value at 25°C in solution (Metcalf and Eddy 2003) is presented in Equation [2]. The dimensionless K_d of NH_4^+ is mainly a function of lagoon-liquid temperature, and TAN concentration present in the liquid manure. The variation of free NH_3 concentration and NH_4^+ concentration with the temperature and pH of the aqueous solution is presented in the Figure 5.1 (Loehr, 1974). It is evident that with increase in temperature the fraction of NH_3 concentration increases. It is also clear that with the increase in pH, the fraction of NH_3 increases and approaches 1.0 at pHs higher than 11. This indicates that if the liquid pH is greater than 11, total loss of TAN as NH_3 gas into the air is theoretically possible. Also, the dissociation constant, K_d of NH_4^+ in clear water as a function of temperature was computed theoretically from Clausius-Clapeyron equation by Jayaweera and Mikkelson (1990) as given equation [3]. Alternatively, Emerson et al., (1975) theoretically modeled the K_d of NH_4^+ in pure water based on the Pk_a method and obtained equation [4].

$$K_d = \frac{[NH_3]_{aq}[H^+]}{[NH_4^+]} \equiv 5.62\times10^{-10} \qquad [2]$$

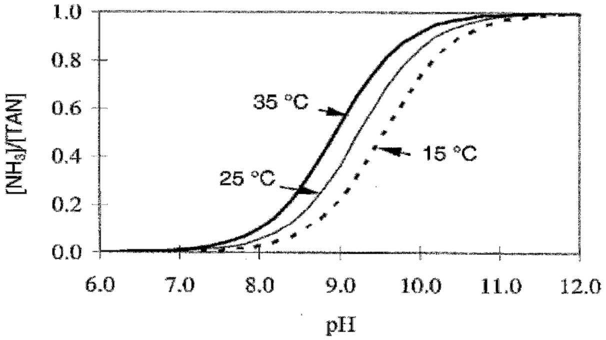

Figure 5.1. Function of NH_3/NH_4^+-equilibrium with temperature and pH in aqueous solutions (Loehr, 1974)

$$K_d = 10^{-(0.0897+2729/T)} \qquad [3]$$

$$K_d = 10^{-(0.09018+2729.92/T)} \qquad [4]$$

According to Snoeyink and Jenkins (1980), equations [2], [3], and [4] are only valid for dilute aqueous solutions where the activity coefficients of the ions approximately one. In concentrated solutions, however, it is important to account for the ionic strength which reduces the activity coefficients and hence K_d of NH_4^+ (Arogo et al. 2002; Clegg and Whitfield, 1995; Snoeynink and Jenkins, 1980). Bell et al., (2007) modeled an expression showing the effect of ionic strength on the K_d of NH_4^+ in saline water and showed that the K_d of NH_4^+ decreases with increase in ionic strength. To correct K_d for ionic strength in concentrated solutions, the activity coefficient of each ion is incorporated in equation [2] as shown in equation [5]. The computation of activity coefficients requires determination of ionic strength (μ) of the solution. Snoeyink and Jenkins (1980) provided an equation [6] for approximating μ using total dissolved solids (TDS).

$$K_d = \frac{\gamma_{NH_3}[NH_3]_{aq}\gamma_{H^+}[H^+]}{\gamma_{NH_4^+}[NH_4^+]} \quad [5]$$

$$\mu = TDS(2.5\times10^{-5}) \quad [6]$$

Some studies have reported the affect of TS concentrations on the K_d of NH_4^+ in livestock manures. The K_d of NH_4^+ in swine manure with 0.25% TS and 400 mg/L TAN at 25 °C was about 52% of the value in deionized (DI) water as reported (Liang et al. 2002). The K_d of NH_4^+ in 1% TS-swine manure was about 0.2 times (20%) the K_d of NH_4^+ in water (Zhang 1992). Ammonia K_d in chicken manure with 3.5-8.5% TS was about 1/6th (16.7%) of the K_d of NH_4^+ in anhydrous NH_3 solution (Hushomoto and Ludington, 1971). Arogo et al., (2002) reported empirical K_d values of swine manure with TS ranging from 0.28% to 0.48% of 0.94, 0.5, and 0.51 compared to K_d of NH_4^+ in water at 15, 25, and 35 °C, respectively. Lower values of K_d of NH_4^+ with TS have been attributed to the solution ionic strength (Laing et al., 2002), and adsorption of TAN on the solids, which inhibits dissociation (De Visscher et al. 2002).

In summary, the ionic strength is approximated from TDS, while the adsorption of TAN is attributed to the total suspended solids (TSS). The TDS and TSS, in general, constitute the total solids (TS). Therefore, the combined effects of both the TDS and TSS, on the K_d of NH_4^+ in livestock wastewater, are represented by the effects of TSS. To the authors' knowledge, no studies exist in the available literature on effect of TS on K_d of NH_4^+ in dairy manure. Such data would greatly enhance development of process models for estimating NH_3 emissions from dairy wastewaters.

The objectives of this study were, therefore, to: (i) empirically determine the effect of temperature on the K_d of NH_4^+ in liquid dairy-manure, (ii) experimentally determine the effect of concentration of TS on the K_d of NH_4^+ in liquid dairy-manure, and (iii) empirically model K_d of NH_4^+in liquid dairy-manure as a function of liquid temperatures and concentration of TS. To achieve these objectives a series of laboratory experiments were conducted in a convective emission chamber (CEC) which enabled precise control of environmental and liquid parameters.

Theoretical Expression of K_d of NH_4^+

There is no standard procedure or a method to directly determine the free NH_3 present in aqueous solutions (Arogo et al., 2002; Emerson et al., 1975). However, determination of TAN (sum of free NH_3 and NH_4^+), is a standard protocol in most wastewater labs. The fraction (α) of free NH_3 in TAN is represented in equation [7] or equation [8] based on equation [1]:

$$\alpha = \frac{[NH_3]}{[NH_3]+[NH_4^+]} \qquad [7]$$

$$\alpha = \frac{1}{1+\frac{[NH_4^+]}{[NH_3]}} \qquad [8]$$

By noting that $[NH_4^+]/[NH_3] = [H^+]/K_d$ and that $pH=-\log_{10}[H^+]$, equation [8] can be simplified and rearranged to give equation [9].

$$K_d = \frac{\alpha}{1-\alpha}10^{-pH} \qquad [9]$$

To model the dissociation constant experimentally using equation [9], the main challenge is determining the value of 'α' for the corresponding pH value. This requires knowing free NH_3, which cannot be determined directly as mentioned earlier. To determine the 'α' value at a particular pH an approach that has been suggested and used in previous studies (Arogo et al., 2002) was adapted. The general equation for volatile gas release from the bulk of any liquid surface is given in equation [10].

$$\frac{dM}{dt} = h_m A(C_L - C_{air}) \qquad [10]$$

To model NH_3 volatilization from liquid into air equation [10] has been rewritten as equation [11] by several authors (Liang et al., 2002; Arogo et al., 1999; Zhang et al., 1992; Hashimoto and Ludington, 1971), where M_{TAN} is mass of NH_3 (kg) in the given liquid of surface area A (m^2); h_m is the overall mass transfer coefficient (m/s); $[NH_3]_L$, and $[NH_3]_{air}$ are the concentrations of NH_3 in liquid and air respectively in g/L.

$$\frac{dM_{TAN}}{dt} = h_m A([NH_3]_L - [NH_3]_{air}) \qquad [11]$$

This equation has further been simplified to equation [12] by noting that, in comparison to the concentration of NH_3 in liquid ($[NH_3]_L$), the concentration of NH_3 in air ($[NH_3]_{air}$) is negligible.

$$\frac{dM_{TAN}}{dt} = -h_m A[NH_3]_L \qquad [12]$$

The negative sign in equation [12] is an indication that the concentration will decrease over a time period and can further be simplified to equation [13] by noting that $M_{TAN} = V \times TAN$ (V is the volume of liquid manure) and substituting αTAN for $[NH_3]_L$, and to equation [14] by integrating equation [13] between 0 and time *t*, and between initial TAN (TAN_0) and TAN at time t (TAN_t).

$$\frac{dTAN}{dt} = -h_m \alpha \frac{A}{V} TAN \qquad [13]$$

$$\text{TAN}_t = \text{TAN}_{L,0}\, e^{-(h_m \alpha \frac{A}{V})t} \qquad [14]$$

Equation [15], which equivalent to equation [14] is the basis for experimental determination of α from measurements of change of TAN with *t* in a CEC. The concentration of TAN remaining with time and a plot of $\ln\frac{TAN_t}{TAN_{L,0}}$ against time t will yield a straight line with a slope, *s*, as given in equation [16].

$$\ln\frac{TAN_t}{TAN_{L,0}} = -h_m \frac{A}{V}\alpha t \qquad [15]$$

$$s = -h_m \frac{A}{V}\alpha \qquad [16]$$

Theoretically (see Figure 5.1), α will approach 1.0 for any pH above 11. This is the basic premise in the experimental determination of α at any other pH (as well as the K_d of NH_4^+) at that pH. To determine the α_{int} at a pH of interest (int), the change of TAN with *t* must be studied at the pH of interest and also at another pH where 'α' value is close to '1' (any pH above 11, in this case will do). The respective slopes are determined at the two conditions to yield equations [17] and [18], respectively.

$$s_{pH(\text{int})} = -h_m \frac{A}{V}\alpha_{pH(\text{int})} \qquad [17]$$

$$s_{pH \geq 11} = -h_m \frac{A}{V}(1) \qquad [18]$$

Dividing equation [17] by equation [18] provides the value for α_{int} as shown in equation [19]. This procedure is repeated within the entire range of conditions of interest to generate data for the empirical modeling of K_d of NH_4^+ as a function of T and TS.

$$\alpha_{pH(\text{int})} = \frac{s_{pH(\text{int})}}{s_{pH \geq 11}} \qquad [19]$$

5.3 Materials and methods

The connective emissions chamber (CEC)

A series of experiments were conducted in a CEC to model the K_d of NH_4^+ as a function of both liquid temperature (T_L) and TS concentrations. Within the CEC, air temperature and air flow velocity were precisely controlled. The CEC consisted of a wind-generator, a flow-controller unit, two screens to effect turbulence, and a sample-chamber. The CEC was replicated from previous similar studies (Arogo et al. 1999, Shaw, 1994, Zhang, 1992). The construction details of the CEC are presented in Figure 5.2 (For convenience, only the test section is given here). A full-size photograph of the CEC is given in the Figure 5.3. The overall dimensions of the CEC were 4.2m × 0.45m × 0.15m (L × W × H). The CEC-walls were built with GI sheet and insulated from inside to avoid any heat transfer from or into the surroundings. The sample test-pan with dimensions 27.9cm × 17.5cm × 4.8cm was placed in a constant temperature water bath to maintain a constant temperature throughout the experimental period. The water bath was able to maintain a constant set temperature within the range of 0–100°C.

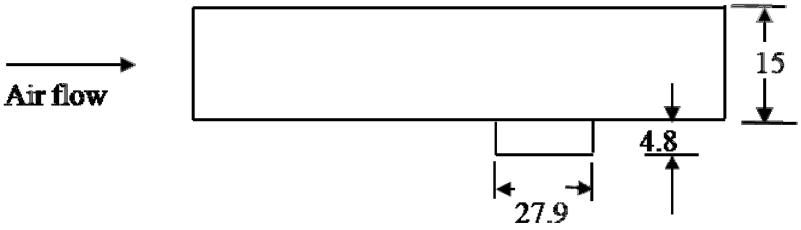

Figure 5.2. A cross-section view of the convective emission chamber test-section (all dimensions in cm but not to scale)

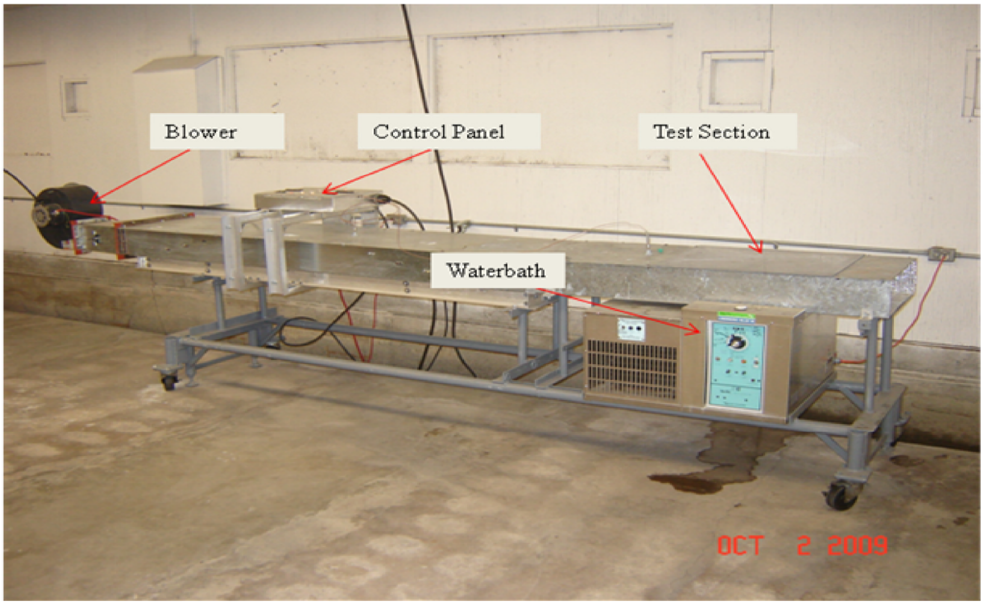

Figure 5.3. A full-size photograph of the Convective Emission Chamber (CEC) in the Lab

Experimental Plan

A series of laboratory experiments in the CEC were conducted to determine K_d of NH_4^+ at TS concentrations ranging from 0.5 to 2.5%, which is the expected range of the TS concentrations in dairy lagoon liquid, and at T_Ls from 5 to 35°C. Each experimental run was conducted with 2.3L sample of test liquid manure with pH adjusted to 9.0 (common pH in dairy manure) using 10M NaOH. The prepared manure sample was poured in the test pan and placed in the constant temperature waterbath. Periodical checking of the temperature of liquid dairy waste in the waterbath ensured that required constant temperature was maintained for all test conditions. A constant air flow velocity over the test liquid was maintained at 1.5 m/s. Before placing the manure pan in the temperature bath, the CEC was operated for at least 20 minutes to stabilize to the test conditions. Once the test conditions were achieved, the manure pan was placed in the waterbath, and again the CEC was run for another 30 minutes to allow the manure liquid adjust to the test conditions. Once manure liquid adjusted to the test conditions, samples were drawn 2 mm below liquid surface for every 30 minutes at 5 random locations (each location 1 mL) of the test pan for 3 hours (0, 30, 60, 90, 120, 150 and 180 min.). To avoid NH_3 loss, 5mL 2M sulfuric acid was added to the drawn samples. In most cases, the samples were analyzed immediately after the experiment using standard methods (APHA 1992). Each condition was evaluated in triplicates at the pH of interest and at a pH of 12. Details of the experimental plan are outlined in the Table 5.1.

Table 5.1. Experimental plan for the determination of ammonium ion dissociation constant in liquid-dairy manure

Run	Solids Content (%)	Liquid Temperature (°C)
1	0.5	25
2	1.0	25
3	1.5	25
4	2.0	25
5	2.5	25
6	1.5	5
7	1.5	15
8	1.5	35

5.4 Data analysis

Regression analyses were performed to analyze the effect of lagoon-liquid temperatures on the K_d of NH_4^+ from 5, 15, 25, and 35°C; and the effect of TS concentrations on the K_d of NH_4^+ from 0.5, 1.0, 1.5, 2.0, and 2.5%. Modeling of K_d of NH_4^+ was done using the Proc NLIN SAS (SAS Institute Inc, 2006) using the entire data set from the environmental and liquid conditions examined in our series of studies. Proc NLIN is the SAS procedure for fitting nonlinear regression models. The data input were the values of K_d of NH_4^+ at four temperatures 5, 15, 25 and 35°C and at five TS concentrations 0.5, 1.0, 1.5, 2.0, and 2.5% W/W.

5.5 Results and Discussions

The exponential decay profiles of TAN from the dairy manure liquid from the start to the end of the test runs (at 25°C and 1.5% TS) are given in Figures 5.4 and 5.5. Figure 5.4 represents the TAN residuals in the dairy manure liquid with time at a pH of 9, while Figure

5.5 represents the TAN residuals in the dairy manure liquid with time at a pH of 12. With reference to equation [19], two test-conditions are required to obtain 'α' of interest, which is necessary for computing the K_d of NH_4^+ at a pH of interest (pH_{int}). The TAN residual curves evidently followed first order kinetics very well with R^2 values of 0.98 and 0.95 for pH 9 and pH 12, respectively. The slope obtained from Figure 5.4 with a pH of 9 was 9.26×10^{-4}, and the slope obtained from Figure 5.5 with a pH of 12 (α=1) was 3.56×10^{-3}. Dividing the slope from Figure 5.4 with the slope from Figure 5.5, the fraction 'α' value was estimated at 0.26. This 0.26 represents the fraction of free NH_3 in TAN in dairy manure liquid with a 1.5% TS, maintained at 25°C, at a pH of 9, and air velocity of 1.5 m/s. The calculated K_d value of NH_4^+ obtained with these parameters is 3.51×10^{-10}. Similar computations were done to determine the K_ds of NH_4^+ at other test-conditions and the results were tabulated (Table 5.2).

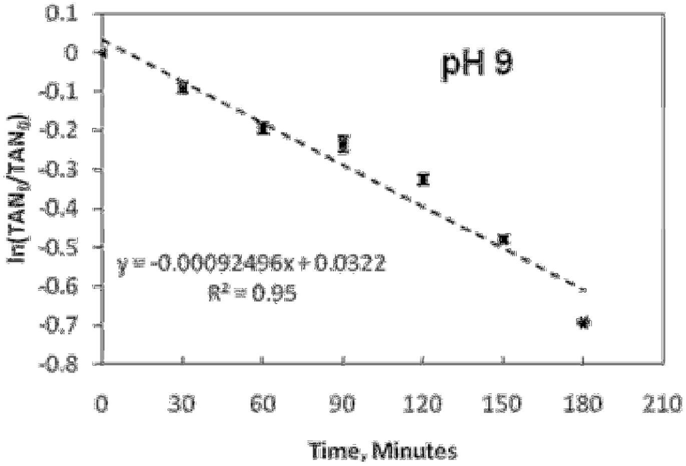

Figure 5.4. Linear decay curves of TAN residuals for the dairy manure liquid at 25°C, 1.5% TS and at a pH 9 (error bars indicate standard deviation from mean)

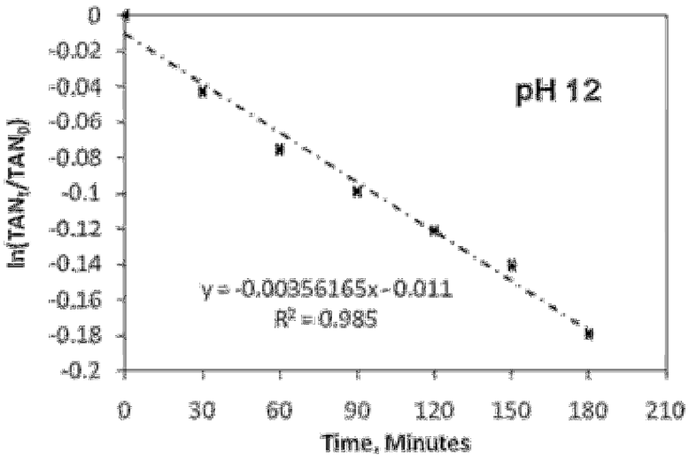

Figure 5.5. Linear decay curves of TAN residuals for the dairy manure liquid at 25°C, 1.5% TS and at a pH 12 (error bars indicate standard deviation from mean)

For comparison; the K_ds of NH_4^+ in liquid dairy manure with 5-35°C, 1.5% TS concentration, and at a pH of 9 obtained from our studies and the K_ds of NH_4^+ reported in the literature are presented in Table 5.2. Arogo et al. (2002) studies were based on swine manure liquid with TS ranging between 0.28 and 0.48% at a lagoon-liquid temperature of 25°C at a pH of 9. Jayaweera and Mikkelsen (1990) values were based on the Clausius-Clapeyron equation, while Emerson et al. (1975) values were based on the pKa = -log K_a (acid dissociation constant) model. The K_ds of NH_4^+ in pure water generated from Jayaweera and Mikkelson (1990) and Emerson et al. (1975) models were also obtained from 5-35°C. From Table 5.2, it is evident that there are no significant differences between the results obtained from Emerson et al. (1975) model compared to the results obtained from Jayaweera and Mikkelsen (1990) model. It is quite apparent also that irrespective of the TS concentration, the K_ds of NH_4^+ in pure water, swine manure, and dairy manure demonstrate similar trends: the K_d of NH_4^+ in all cases increased with the increase in temperature. The K_ds of NH_4^+ in dairy manure liquid with 1.5% TS at 5, 15, 25, and 35°C were respectively 1.17, 0.87, 0.61, and 0.54 times those of theoretical K_ds of NH_4^+ in pure water at similar temperatures conditions. The change in the ratios of the K of NH_4^+ in dairy manure slurry and in pure water, at a constant TS level and varying temperature, indicate interaction between temperature and concentration of TS. The latter observation strongly suggests models of K_d of NH_4^+ in liquid-dairy manure must consider the simultaneous effects of the concentration of TS and temperature.

Table 5.2. Theoretical and experimental K_ds of NH_4^+ from current and previous studies.

Temp. °C	Jayaweera and Mikkelsen (1990) (water) $\times 10^{-10}$ $K_d = 10^{-(0.0897+2729/T)}$	Emerson et al. (1975) (water) $\times 10^{-10}$ $10^{-(0.09018+2729.9/T)}$	Arogo et al. (2002) $\times 10^{-10}$[†]	Current studies $\times 10^{-10}$[‡, a]
5	1.26	1.25	- -	1.47±0.06
15	2.75	2.73	2.55±0.19	2.39±.09
25	5.72	5.67	3.39±0.22	3.51±0.13
35	11.33	11.2	6.75±0.78	6.06±0.11

[†] Swine manure with total solids ranging 0.26- 0.48% (air flow velocity over pan 1 m/s)

[‡] Dairy manure with total solids 1.5% (air flow velocity over pan 1.5 m/s)

[a] K_d values obtained using the same procedure as explained in Figures 5.5 & 5.6 at each temperature

Effect of liquid temperature on K_d

The effect of T_L on the K_d of NH_4^+ was further analyzed using the classical van't Hoff model shown in Equation [20] (Silbey et al., 2005), where K, equilibrium constant; ΔH^{Θ}, change in enthalpy (constant), J/mole; ΔS^{Θ}, change in entropy (constant), J/mole; R, universal gas constant, 8.314 J/mole.K, and T, temperature, K. In general, the van't Hoff model provides a physical relationship between K_d and temperature for dissociating chemical compounds. A graphical presentation of the van't Hoff equation fitted using the data obtained from this study is presented in Figure 5.6. It is explicit that the effect of temperature on the K_d of NH_4^+ in dairy manure can be presented by a simple van't Hoff model given the strong correlation coefficient, R^2, of 0.99. The equation generated in Figure 5.6 can thus reliably be used to correct K_d for temperature or for prediction of K_d values within the temperature range investigated in our study.

$$\ln K = -\frac{\Delta H^{\Theta}}{RT} + \frac{\Delta S^{\Theta}}{R} \qquad [20]$$

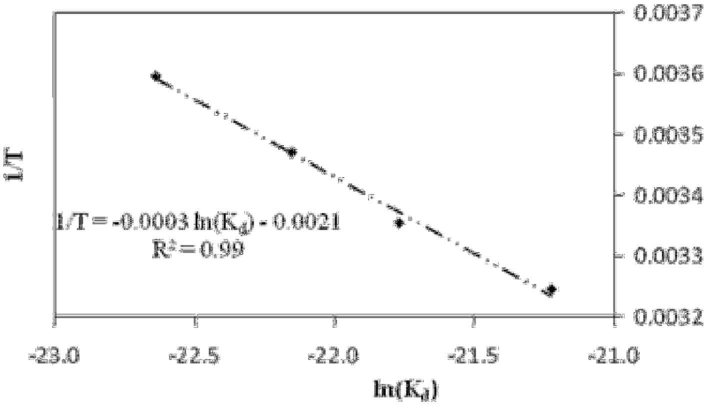

Figure 5.6. A linear regression fit of the van't Hoff model based on the experimental data obtained in this study

Effect of TS concentrations on K_d

The K_ds of NH_4^+ in liquid-dairy manure at different solids concentrations are presented in the Table 5.3. A linear regression plot showing the effect of TS concentrations on the K_d of NH_4^+ in liquid-dairy manure, on the other hand, is presented in Figure 5.7. The K_d of NH_4^+ in the liquid-dairy manure decreased linearly (R^2 =0.99) with increase in the concentration of TS. This result further demonstrates that presence of solids and the higher ionic strength in dairy manure inhibit dissociation of NH_4^+ and that the more the solids (or conversely the higher ionic strength), the more the inhibition. The K_d values of NH_4^+ in the dairy manure liquid with 1.5% TS concentrations were 117%, 87%, 61%t, and 54% compared to the theoretical K_ds of NH_4^+ in pure water at 5, 15, 25, and 35°C, respectively. It is evident that with constant TS concentrations (1.5%), the ratios of K_ds of NH_4^+ in dairy manure with K_ds of NH_4^+ in pure water decreased with increase in the T_Ls. This clearly explains that TS concentrations will have surely effect on the K_ds of NH_4^+. It also could be concluded that the effect of TS concentrations increases with increases in lagoon-liquid temperatures.

Table 5.3. K_ds of NH_4^+ at different total solids concentrations

Solids Conc.% W/W	$K_d \times 10^{-10}$
0.5	4.08±0.36
1.0	3.60±0.18
1.5	3.51±0.13
2.0	3.36±0.29
2.5	3.06±0.28

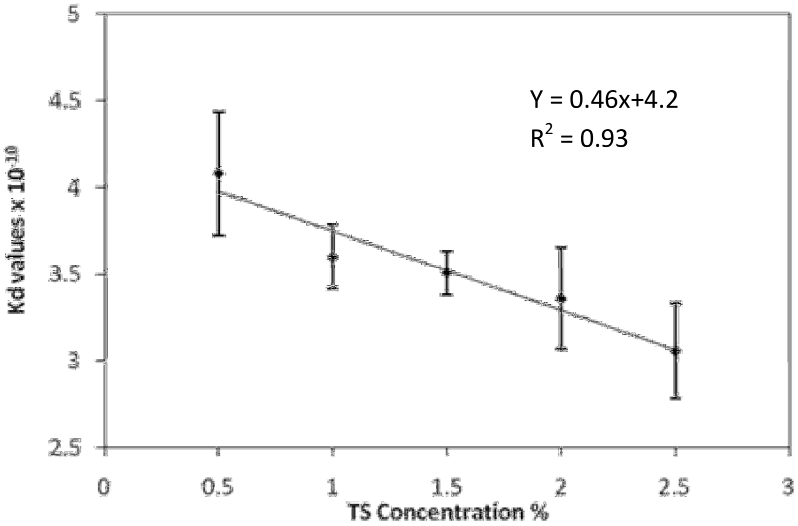

Figure 5.7. Effect of total solids (TS) concentrations on K_ds of NH_4^+ in liquid-dairy manure (error bars indicate standard deviation from mean)

Model of K_d of NH_4^+

To model the K_d of NH_4^+ based on T_Ls and TS concentrations, we adopted the pKa method followed by Emerson et al. (1975), which models K_d using pKa as given in equation [19].

$$K_a = 10^{-pKa} \qquad [21]$$

In formulating equation [22], Emerson et al. (1975) noted that the K_d of NH_4^+ increases with increase in temperature. This assumption was verified in the current studies (Figure 5.6). The effect of TS concentrations on K_d of NH_4^+ formulated in equation [23] was based on the data gathered in the current study (Figure 5.7) and also from previous studies (Arogo et al., 1999; Zhang, 1992), where A, B, C, and D are constants.

$$pK = A + \frac{B}{T} \qquad [22]$$

$$pK = C + D(TS) \qquad [23]$$

The K_ds of NH_4^+ obtained at different TS concentrations, and different T_Ls were the input to the Non-linear regression procedure (Proc NLIN) of Statistical Analysis System program 9.1.3 (SAS institute Inc. 2006). From the results of the Proc NLIN, the respective constants were obtained resulting in the empirical model presented in equation [24] whose R^2 value of 0.97 indicated a good fit to the experimental data. The empirical model seems physically sound because it displays the expected relationships between K_d and TS concentration and also with T_L, i.e. higher TS decreases K_d while higher T_L increases K_d.

$$K_d = 10^{-(2.0153+1.208*TS)*(1.8944+819.8/T)} \qquad [24]$$

Where TS = total solids concentration W/W, 0.5% means, TS = 0.005, and T = temperature in Kelvin. A comparison of actual values and model predicted values of K_d of NH_4^+ at different T_Ls (5, 15, 25 and 35°C) and at the TS concentration of 1.5% is shown in Figure 5.8. In addition, a comparison of actual values and model predicted values of K_d of NH_4^+ at different TS concentrations (0.5, 1.0, 1.5, and 2.5%) at 25°C is presented in Figure 5.9. In both cases, the actual values compared very well with the model predicted values, further illustrating the good fit of the nonlinear regression model to the experimental data.

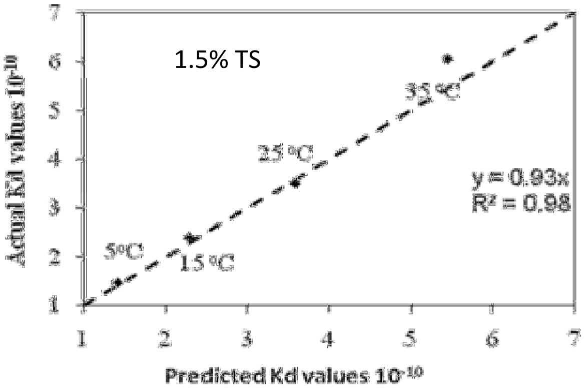

Figure 5.8. A comparison of actual and model predicted K_ds of NH_4^+at different temperatures and 1.5% TS concentration

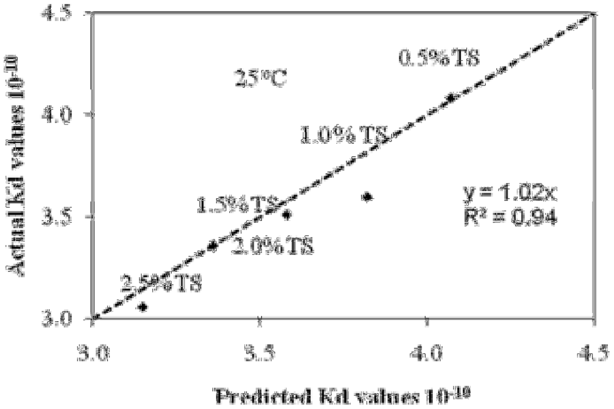

Figure 5.9. A comparison of actual and model predicted K_ds of NH_4^+at different TS concentrations at 25°C

A comparison of K_ds of NH_4^+ in dairy manure as predicted by our model at T_Ls 5, 15, 25, and 35°C with the K_ds of NH_4^+ predicted by the Emerson et al., 1975 in pure water at temperatures 5, 15, 25, and 35°C is given in the Figure 5.10. Both models compared well linearly with an R^2 value of 0.99. The predicted K_ds of NH_4^+ in pure water were increased 2.18 (5-15°C), 2.08 (15-25°C), and 1.98 (25-35°C) times according to Emerson et al., (1975) model. The calculated K_ds of NH_4^+ in pure water increased 2.19, 2.09, and 1.99 times from 5-15, 15-25, 25-35°C respectively using the van't Hoff equation. However, predicted K_ds of NH_4^+ from our model increased approximately 1.6 times for every 10°C rise in temperature.

These results showed that our model predictions are in agreement with the predictions from Emerson et al., (1975) theoretical model when the effects of solids (and ionic strength) are taken into account. Inhibition of K_d of NH_4^+ by the TS concentrations and the higher ionic strength inherent in the dairy manure most probably explains the fact that the K_d of NH_4^+ in dairy manure did not double in accordance with Emerson et al, 1975 model or with van't Hoff model for every 10°C rise in temperature; exhibited in pure water. The Emerson et al.'s (1975) model in conjunction with the regression model can thus also be used to reliably predict the K_ds of NH_4^+ within the conditions examined in this study.

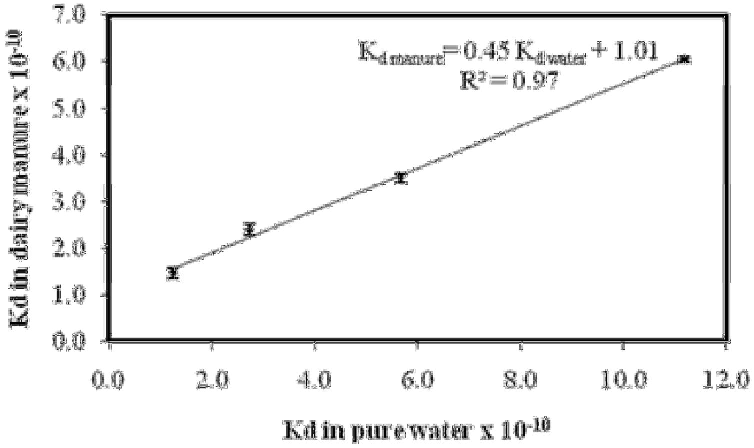

Figure 5.10. A comparison of our model predicted K_ds of NH_4^+ in dairy manure with predicted K_ds of NH_4^+ in pure water by Emerson et al., (1975) model at 5, 15, 25, and 35°C (error bars indicate standard deviation from mean)

5.6 Summary and conclusions

A series of laboratory experiments were conducted in a convective emissions chamber to model the K_d of NH_4^+ at four T_Ls levels (5, 15, 25, and 35°C) and at five levels of TS concentrations (0.5, 1.0, 1.5, 2.0, and 2.5%). The conclusions drawn from these studies are:-

1) When the effect of T_L is considered alone, the K_d of NH_4^+ increased with increase in temperature. From 5 to 35°C, the K_ds increased by approximately 1.6 times for every 10°C rise in temperature. The K_d of NH_4^+ temperature dependence in the liquid dairy

manure can be described using a simple Van't Hoff model. This indicates that the increase in temperature results in more fraction of unionized NH_3 which can in turn result in increased NH_3 emissions into the surroundings.

2) The K_d of NH_4^+ decreased linearly with the concentration of TS indicating an increasing inhibition of NH_4^+ dissociation with increasing TS level in liquid dairy manure.
3) The empirical model (equation [24]) developed for K_d of NH_4^+ as a function of temperature and the concentration of TS had an R^2 value of 0.97 indicating that the model was strongly consistent with the experimental data. This model is, therefore, reliable for determination of the K_d of NH_4^+ within the experimental conditions covered in this study (i.e. in the range 0.5 to 2.5% TS concentrations, and in the temperature range of 5 to 35°C).
4) In general, our empirical model on the effect of temperature on the K_d of NH_4^+shows good agreement with Emerson et al.'s (1975) theoretical model predicting K_d of NH_4^+ in pure water (R^2 of 0.99: Figure 5.10). However, the absolute values of the K_d of NH_4^+ in the liquid-dairy manure were less than those in pure water: this difference is attributed to the inhibition of NH_4^+ dissociation by presence of solids in the liquid-dairy manure.
5) Models of the K_d of NH_4^+ in livestock wastewaters need to consider both the effects of wastewater temperature and total solids content to enhance model reliability.
6) In order to initiate ammonia emissions mitigation strategies based on the effects of solids and/or ionic strength on the K_d of NH_{4+} in dairy manure, it important to conduct further studies to delineate the effects of solids from those of ionic strength.

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CHAPTER SIX

A Process-based Model for Ammonia Emissions from Storages of Flushed Dairy Manure

6.1 Abstract: Ammonia (NH_3) is one of the major gaseous pollutants emitted from livestock facilities. Estimates indicate that the largest portion (about 75-80%) of the total nitrogen entering a dairy facility is lost as NH_3 from manure storages; such as anaerobic lagoons. Direct measurements of NH_3 emissions from these storage structures are not only tedious but also quite complex and expensive exercises. Process-based models offer an alternative cost-effective approach of making emissions estimations. This research coupled theoretical and empirical analyses of NH_3 emissions mechanisms to increase the reliability of NH_3 emission process-based models. A process-based model was developed to quantify NH_3 emissions from dilute dairy manure via incorporation of two newly developed empirical sub-models of: the overall mass transfer coefficient (K_{oL}) of NH_3 from liquid dairy manure; and the dissociation constant (K_d) of ammonium ion (NH_4^+) in liquid dairy manure. The K_{oL} was modeled based on lagoon-liquid temperature (T_L), air velocity, air temperature, and total solids (TS) concentrations. The K_d was modeled based on T_L, and TS concentrations. The model predictions were validated with directly measured NH_3 emissions using an open-path ultra-violet differential optical absorption spectroscopy (UV-DOAS) technique. Directly measured NH_3 emission fluxes from our study lagoon ranged from 16.1 to 41.2μg/m^2/s, which compared well against our model predicted fluxes with a normalized mean error (NME) of 15%. Sensitivity analyses showed NH_3 emission is most sensitive to the lagoon-liquid temperature compared to the other factors (air temperature, air velocity, and total solids concentrations) examined in this study.

Keywords: Ammonia, emission fluxes, dilute dairy manure, manure storages, UV-DOAS, backward Lagrangian scholastic (BLS).

6.2 Introduction

Agricultural activities, including livestock operations, are estimated to contribute about 80% of ammonia (NH_3) emissions in the USA (EPA 2002) and about 90% in the Europe (Bujjsman et al., 1987). Ammonia can be emitted from any part of the animal operations including animal housing, bedding, solids and liquids separation areas, manure storage facilities (under floor pits and anaerobic lagoons), composting facilities, and from land application of manure on soil as a fertilizer (Liang et al., 2002). An ICL and IDEAL (2005) report indicated that approximately 70-85% of the total nitrogen (Total-N) entering dairy facilities will be lost through gaseous NH_3 emissions from an anaerobic dairy waste lagoon.

The negative impacts of volatilized NH_3 to human and animal health and to the environment, in general, are well recognized. Eutrophication caused by NH_3 has deleterious ecological effects. Beyond unpleasant odors, extended exposure to NH_3 emissions may cause irritations in humans or permanent damages to the respiratory tissues of confined animals (Gay and Knowlton, 2005). Ammonia is a precursor to the formation of respirable particular matter ($PM_{2.5}$), which also impairs visibility. The $PM_{2.5}$ is currently regulated in the US-EPA Clean Air Act (CAA) under the National Ambient Air Quality Standard (NAAQS) regulations (Rumburg, 2006). Reduced NH_3 emissions may thus mitigate $PM_{2.5}$ emissions.

To control NH_3 emissions and set standards; technologies are needed to estimate NH_3 emissions in a cost-effective way. Continuous direct measurement of NH_3 emissions, however, requires expensive instrumentation and is labor intensive. An alternative method to estimate NH_3 emissions in a cost-effective way is process-based emission models. In a recent study, Rumburg et al. (2008) modeled NH_3 emissions from an anaerobic dairy waste lagoon and compared model predictions with direct measurements. From their results, Rumburg et al. (2008) reported a normalized mean error (NME) of 21% when empirical constants of K_{oL} values of NH_3 (reported by Ni, 1999) were used compared to a NME of 120% with theoretical constants in the process model. Their results demonstrated the inadequacy of theoretically derived constants and strongly suggested use of empirically determined constants to improve the reliability of the process based model.

This overall goal of this research was to couple theoretical and empirical modeling approaches to develop a credible process-based model of NH_3 emissions from dairy lagoons. The specific objectives of the research were to: i) incorporate two newly developed empirical sub-models (the K_d of NH_4^+ and the K_{oL} of NH_3) in a process model for NH_3 emissions from dairy manure storages., ii) acquire direct NH_3 emissions data from an anaerobic dairy waste lagoon for model validation, and iii) perform sensitivity analyses of the model to identify critical model parameters.

Theory and Model Development

A generic process model for NH_3 emissions from bulk liquid, such as anaerobic dairy waste lagoon, is presented in Equation [1] (Ni 1999): where: Q_a = Ammonia flux g/s; K_{oL} = Overall mass transfer coefficient, m/s; A = Area of emitting surface, m^2; $[NH_3]_L$ = Free NH_3 concentration at the lagoon liquid surface, g/m^3; and $[NH_3]_a$ = Ammonia concentration in air, g/m^3. In comparison to $[NH_3]_L$,, $[NH_3]_a$ is negligible and is usually omitted from NH_3 emissions flux calculations. When $[NH_3]_a$ is eliminated in Equation[1] this expression is rewritten as Equation[2]. The two key parameters in this equation are the K_{oL} and the $[NH_3]_L$. The K_{oL} is a function of four manure and environmental factors: air temperature (T_{air}), liquid temperature (T_L), air velocity (V_{air}), and total solids (TS) concentrations. A sub-model considering these environmental factors is required to derive K_{oL} of NH_3. The K_{oL} of NH_3 in dairy manure, based on these factors, was empirically modeled by the authors in previous studies (Chapter 4), in a series of convective emissions chamber (CEC) experiments. Based these previous studies, the K_{oL} of NH_3 was found to be directly proportional to $T_{L,}$ and V_{air}; and inversely proportional to T_{air} and TS concentrations as presented in equation [3].

$$Q_a = K_{oL}A([NH_3]_L - [NH_3]_a) \qquad [1]$$

$$Q_a = K_{oL}A([NH_3]_L) \qquad [2]$$

$$K_{oL} = 4.85\times10^{-11}\frac{(T_L)^{9.7}(V_{air})^{0.34}}{(T_{air})^{8.02}(TS)^{0.26}} \qquad [3]$$

The component of NH_3 in solution (i.e., $[NH_3]_L$) depends on the dissociation constant (K_d) of NH_4^+ in the lagoon liquid. The K_d of NH_4^+ is thus required to estimate the fraction of free NH_3 present in liquid dairy manure. The K_d of NH_4^+ in turn is a function of T_L and TS concentrations and was empirically modeled in earlier work using data from a series of CEC experiments (Arogo et al., 1999). The K_d of NH_4^+ was directly proportional to the lagoon-liquid temperature (T_L), and inversely proportional to TS concentrations. An equation for estimating K_d of NH_4^+ in dairy manure, within the conditions examined in this study (Chapter 5), is presented in Equation [4].

$$K_d = 10^{-(2.0153+1.208*TS)*(1.8944+819.8/T_L)} \qquad [4]$$

6.3 Materials and Methods

Data for model validation were collected at an anaerobic dairy waste lagoon located at Washington State University Knott Research Dairy Center in Pullman, Eastern Washington. The lagoon surface area is approximately 5900m^2. This dairy has about 250 cows (milking cows and heifers) and approximately 80 calves and has a manure-flushed handling system. The dairy cows are housed in concrete-floor freestall barns. The wastes (feces, urine, and from bedding, milking parlor waste water, etc.) produced are scraped into manure pits. This waste is flushed from the pits using recycled wastewater to a solids separator. In the solids separator solids with greater than 0.3 cm diameter are removed. The wastewater then is pumped to a high solids lagoon where solids settle via gravity. The supernatant from the high solids lagoon next flows into the low solids lagoon (5900 m^2). The supernatant water from low solids lagoon is used as recycled wastewater for flushing the scraped waste from the pits.

Direct Ammonia Emissions Measurements

A ultra-violet differential optical absorption spectroscopy (UV-DOAS) system (UV sentry, Cerex Monitoring Solutions Inc., Atlanta GA) was used in this study for direct measurements of NH_3 emissions. The UV-DOAS system consisted of an UV-light emitting source which emits UV-light at several wavelengths, a receiver to receive the residual light, a 3-D sonic anemometer to acquire weather data (3-dimensional wind velocity, air temperature, and wind direction), and a personal computer (PC) for data processing.

The UV-DOAS system has several advantages such as continuously unattended real time concentrations measurement and does not need any collection devices such as canisters or gas sampling bags, ability to measure for an indefinite period of time, high accuracy, and importantly no need for calibration and can quickly be setup (the instrument set-up time at the lagoon takes approximately 30 minutes). This instrument, however, needs an up-wind background concentration measurement before actually measuring the field concentrations. Before the actual direct data acquisition of NH_3 emissions from an anaerobic lagoon, it was ensured that the up-wind background concentration was obtained in the field.

The UV-DOAS employs a technique of averaging the spectroscopic absorption of several molecular species in the atmosphere over a path length within ranges of a few meters to kilometers. This instrument works based on the Beer-Lambert law. As illustrated in Figure

6.1, the UV-DOAS consists of a Xenon light source emitting a broad beam of UV into the atmosphere. Different gases absorb light at different wavelengths so the receiver system detects the level of residual UV light intensity not absorbed by the trace gas pollutants in the atmosphere. This instrument uses a built in database of pre-calibrated absorption spectra of NH_3 signal to quantify the concentrations of NH_3 in air. Ammonia molecules generally absorb UV-light in the range of 200-350 nm. With a minimum detection limit of 1 part per billion by volume (ppbv) and no overlapping absorbencies of different tracer gases, the UV-DOAS is sufficiently accurate for detecting NH_3 concentrations in the air.

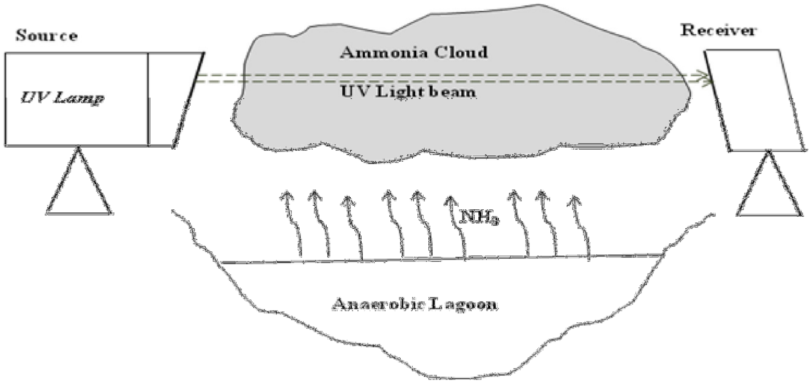

Figure 6.1. UV-DOAS field set-up

The UV-DOAS emitter and receiver were set-up approximately 10 m downwind of the anaerobic dairy waste lagoon #2. The path-length was 85m between the light emitter and receiver. The instrument was set-up to sample NH_3 concentrations every 5 minutes. The meteorological data including wind velocity, wind direction, and air temperature were acquired using 3-D sonic anemometer (RM Young) also every 5 minutes. The NH_3 concentrations data file from the UV-DOAS and meteorological data set from 3-D sonic anemometer were merged into a single data set file using proprietary Cerex software (Cerex monitoring solutions Inc). The merged data file was then analyzed by WindTrax software provided by the vendor to calculate the emission fluxes using the Backward Lagrangian Stochastic (BLS) dispersion modeling technique (Thunder Beach Scientific, 2009, Version

V.2.0.8.3). WindTrax was programmed to calculate the emission fluxes averaging over 15 minutes.

The lagoon-liquid temperature (T_L) was monitored every half hour using a hand held mercury thermometer. Samples of the lagoon liquid were collected during to the direct NH_3 emissions data acquisition and were later analyzed immediately in the laboratory for TS and TAN concentrations using standard methods (APHA, 1992), upon return from the field. The lagoon-liquid pH was determined with a pH meter in the laboratory. The ambient environmental conditions T_{air} and V_{air} were obtained from 3-D sonic anemometer.

6.4 Data Analyses

Validation of model predictions:

Model validation was performed by comparison of model NH_3 emissions predictions with directly measured NH_3 emissions. The fitness of the model predictions to the actual measurements was estimated using the normalized mean error (NME) method. The expression for the NME is presented in Equation [5]: where 'n' is the number of data points and X_{mod} and X_{mea} the modeled and measured NH_3 fluxes (µg/m^2/s), respectively.

$$NME = \frac{\sum_{1}^{n} \left| X_{\mathrm{mod}} - X_{mea} \right|}{\sum_{1}^{n} X_{mea}} \times 100\% \qquad [5]$$

Sensitivity Analysis:

Sensitivity analyses of the developed model to predict NH_3 emission fluxes from anaerobic dairy lagoon were performed using a simple spreadsheet (MS Excel). These analyses were performed in two ways. First, the overall sensitivity of the model was evaluated by varying all model parameters simultaneously from their respective midpoints of each parameter range (i.e. the midpoint to lowest and highest points in the respective range). Second, the sensitivity of the model was evaluated by varying individual model parameter one at a time from its midpoint to lowest and highest points in the respective parameter's range; while holding all other parameters constant.

6.5 Results and Discussions

Ambient Air Ammonia Concentrations and Ammonia Fluxes on a Typical Day

Ammonia concentrations in the ambient air 10m downstream of the anaerobic lagoon and the pattern of lagoon liquid temperature during a typical day time from 11.00 to 16.30 hrs on September 22, 2009 are presented in the Figure 6.2. The NH_3 emission fluxes for the same time period computed with WindTrax software and BLS technique is presented in Figure 6.3. The prevailing wind direction for this day was east. The T_L at the beginning of the day was 16 °C (T_{air} at 22.4°C), which rose to 24.0°C (T_{air} at 26.3°C) at the 16.30th hour of the day. During this period, the T_L increased by 8°C while the T_{air} increased by 3.9°C. At the beginning of the day the T_L was 16°C (T_{air} at 22.4°C) and as the day advanced, the T_L increased to 24.0°C (T_{air} at 26.3°C). It is clear from Figure 6.2 that ambient-air NH_3 concentrations increased with the increase in the T_L. In general, the changes in TS concentrations and the pH of the lagoon-liquid will be negligible during such a typical day and the effect of these factors on NH_3 emissions for the period can be neglected. The observed dips in the plots of NH_3 concentrations and fluxes (Figures 6.2 and 6.3) are probably due to the changes in the prevailing wind direction.

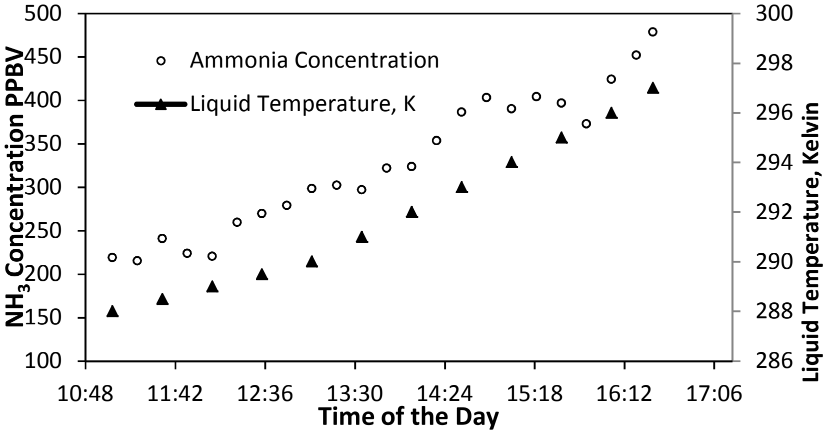

Figure 6.2. Ammonia emission concentrations pattern during the time of the day measured with UV-DOAS

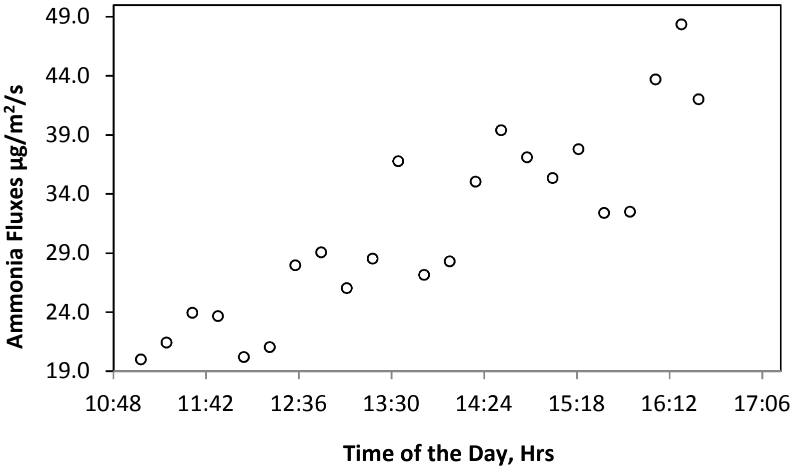

Figure 6.3. Ammonia emission fluxes pattern during the time of the day estimated by WindTrax software with BLS technique

Model Validation

A comparison of 30 measured (averaged over 15 minutes) and 30 model predicted NH_3 fluxes from an anaerobic dairy waste lagoon is shown in Figure 6.4. These measured fluxes were collected during a winter month (December 2008) and a fall month (September 2009). The measured and predicted NH_3 emission fluxes compared well with a normalized mean error (NME) of 15%. This NME compared also well with the value reported NME 21% by Rumburg (2008). Rumburg (2006) used both theoretical and empirical values reported in the literature. Using empirical constants reported by Ni (1999) he obtained an NME of 21%

between measured and predicted emissions. When he used theoretically derived constants from Mackay and Yeun (1983) work, a NME of 120% was observed between the predicted and measured emissions. Our studies concurs with Rumburg et al (2008) studies that estimations of NH_3 emissions using process-based models that use empirically derived mass transfer coefficient and dissociation constants are more reliable than the ones using theoretically derived values. This observation is not totally unexpected because while empirical values consider the complex nature of manure systems, theoretically derived values do not account for this complexity.

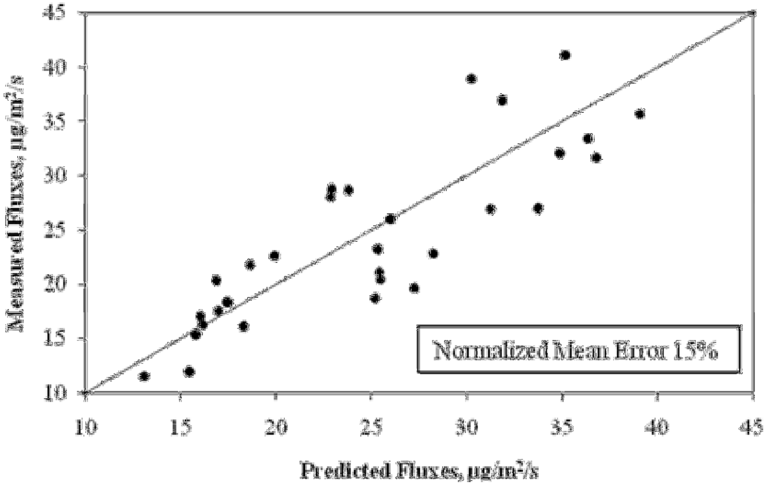

Figure 6.4. Comparison of UV-DOAS measured and predicted NH_3 emission fluxes from an anaerobic dairy waste lagoon

The NH_3 fluxes from the anaerobic dairy lagoon in this study, for a typical day, ranged from 1.72 to 3.55 g/m²/day depending on the time of the day. These fluxes (15 minute averages) were estimated assuming that if the same conditions prevail throughout the day. The measured fluxes reported in the literature from several studies ranged from 0.13 g/m²/day in winter to 13 g/m²/day in summer (Vaddella et al., 2009; Rumburg et al., 2008; McGinn et al., 2008; Smith et al., 2007; Mutlu et al., 2004). Using UV-DOAS technique, de Haro Marti et al., (2007) conducted a study estimating NH_3 fluxes from an anaerobic dairy waste lagoon in south-central Idaho. They estimated average NH_3 fluxes ranging from 1.6 to 2.5 g/m^2/day in winter to summer, respectively. The fluxes from the lagoon in our study were thus well within the range of fluxes reported in the literature.

Sensitivity analysis of the NH_3 emission prediction model

The environmental factors (T_{air}, and V_{air}), and manure properties (T_L, and TS concentrations) are the model parameters that affect NH_3 emission fluxes from an anaerobic dairy waste lagoon or similar manure storage structures. The sensitivity analysis was, therefore, performed to evaluate the sensitivity of predicted NH_3 emission fluxes (Equation [2]) by varying these factors and results are presented in Tables 6.1 and 6.2. When all the model parameters were simultaneously decreased from their respective midpoints to the lowest possible level, NH_3 emission fluxes decreased by 64.0%. Similarly, when all the model parameters were simultaneously increased from their respective midpoints to the highest possible level, NH_3 emission fluxes were increased by 117.2%. This shows that on a same day, there is a greater potential for either increase or decrease of NH_3 losses from an anaerobic dairy waste lagoon.

Table 6.1. Sensitivity analysis of model predicted NH_3 fluxes

Parameter/ Range	**T_L, °C**	**TS, %**	**V_{air}, m/s**	**T_{air}, °C**	**Predicted NH_3 fluxes μg/m^2/s**	**Sensitivity %**
Below Midpoint	5	0.5	0.5	15	9.2	-64.0
Above Midpoint	35	2.5	4.0	35	55.5	117.2

T_L = Lagoon-liquid temperature; T_{air} = Air temperature; V_{air} = Air velocity; TS = Total solids concentration w/w

The model indicated sensitivity to all the factors considered, in descending order, to be as followed: T_L, V_{air}, TS concentrations, and T_{air} respectively (Table 6.2). The effective sensitivity of the model to both T_L and V_{air} was, therefore, higher than the effective sensitivity of the model to both the TS concentrations and T_{air}; within the ranges of these respective parameters in this study. The effect of sensitivity of T_L on the model predicted NH_3 fluxes was the highest evidently showing that warmer locations will result in higher NH_3 losses from anaerobic dairy lagoons. The sensitivity of the model to T_L was higher above the midpoint (200.0 %) than below the midpoint (-69.9%). The model was more sensitive at the lower range of V_{air} (-51.1%) than at the higher range of V_{air} (22.9%). With respect to TS content, the model indicated higher sensitivity at lower TS content (40.0 %) than at higher TS contents (-21.6%). Finally, the model was more sensitive at lower T_{air}s (31.5 %) than the higher T_{air}s (-23.2%).

Table 6.2. Effect of each model parameter on the sensitivity of model predicted NH_3 fluxes

Parameter	Point in the Range		NH_3 fluxes $\mu g/m^2/s$	Sensitivity %
	5	L	7.7	-69.9
T_L, °C	20	M	25.6	--
	35	H	76.6	200.0
	0.5	L	38.6	-51.1
V_{air}, m/s	2.25	M	25.6	--
	4.0	H	19.7	22.9
	15	L	15.3	31.5
T_{air}, °C	25	M	25.6	--
	35	H	31.1	-23.2
	0.5	L	33.6	40.0
TS Content, %	1.5	M	25.6	--
	2.5	H	19.6	-21.6

L = Lowest; M = Midpoint; H= Highest

6.6 Summary and Conclusions

Ammonia emissions from an anaerobic dairy waste lagoon were modeled using a generic mechanistic NH_3 emissions equation. Two newly developed empirical sub-models for K_d and K_{oL} were incorporated in the process model to improve the model's reliability. For model validation, direct NH_3 emission fluxes were measured using a ultra-violet optical absorption spectroscopy technique. Comparisons based on NME analysis were made between the model predicted and measured fluxes and the conclusions drawn are:-

1. The measured NH_3 fluxes increased linearly with increase in the day's temperature and ranged from 19.97-41.1 $\mu g/m^2/s$. The corresponding predicted emissions increased from 25.7-35.2 $\mu g/m^2/s$. The NME between the model-predicted values and the measured values was 15%. These NH_3 fluxes compared well with the results from previously reported studies.
2. The sensitivity analyses showed that the emission fluxes are directly proportionally sensitive to the T_L and V_{air}. The fluxes, on the other, were inversely proportional to both TS concentrations and T_{air}. The effective sensitivity of the model to both T_L and V_{air} was, however, higher than the effective sensitivity of the model to both the TS concentrations and T_{air}; within the ranges of these respective parameters in this study.
3. The model was greatly sensitive in the above midpoint range than in the range below midpoint when all the model parameters were varied simultaneously from midpoint to each way.
4. Each model parameter one at a time was varied from midpoint to lowest and highest points in the respective parameter's range holding all other parameters constant. The model sensitivity for T_L was higher in the above-midpoint range than the below-midpoint range. The model had greater sensitive to V_{air} at the below-midpoint range than the above-midpoint range. The model had higher sensitivity at the range below

midpoint than in the range above midpoint for T_{air}. The model was more sensitive in the range below midpoint than in the range above midpoint for TS content.

6.7 Acknowledgements

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CHAPTER SEVEN

Summary, Conclusions, and Future Work

This research consisted of an ammonia (NH_3) emission management component and an NH_3 emission modeling component; from dairy manure storages. In the emissions management part, laboratory scale experiments were conducted to compare NH_3 emissions mitigation from two commonly manure handling systems: manure flushing and scraping. In addition, the effectiveness of urine-feces separation prior to waste storage was also studied. In the emissions modeling component, a series of laboratory scale experiments were conducted in a convective emissions chamber (CEC) to develop two critical constants that were necessary to improve the reliability of NH_3 emission process model. Field measurements were finally conducted at a full-size anaerobic dairy waste lagoon to obtain data for validation of the developed NH_3 emissions model. Summaries and conclusions of these studies as well as suggestions for future studies are provided next in this chapter.

Part-I: Ammonia Emissions Management

Study 1. Scrape System versus Flush System

A series of bench scale experiments were conducted to quantify and compare NH_3 losses from simulated storages of scraped manure and flushed manure based on the exposed-surface-area to volume ratio (ESAVR) and also based on the exposed surface area only. The cumulative NH_3 emissions and fluxes from reconstituted and actual flushed manures were not significantly different at $\alpha=0.05$. Therefore, the assertions (diluting a mix of urine to feces in the ratio of 1.00:1.68 with 2.5 times tap water on weight basis) made for reconstitution of flushed manure from separately collected urine and feces were valid. The cumulative NH_3 emissions and NH_3 fluxes from simulated storages of scraped and flushed manure with same ESAVRs were not statistically different at $\alpha=0.05$. This result thus indicated no advantage of either scraping manure or flushing manure if the designs of the storages of the flushed and the scraped manure were based on the same ESAVR. Emissions of NH_3 from post-collection storages of flushed and scraped manure in similar storages (same exposed surface area) indicated statistically significantly different emissions at $\alpha=0.05$. Ammonia emission from the storage of scraped manure was higher than that from storage of flushed manure. This result indicated that if the post collection storages of both the scraped and flushed manure were geometrically identical, the storage of scraped manure will result in more NH_3 emissions than the storage of flushed manure.

Study 2. Urine-feces Separation Strategy

Laboratory scale simulation studies were conducted to evaluate NH_3 emissions from post-collection storages of three waste streams: i) idealistically separated feces and urine (no contact between urine and feces), ii) realistically separated urine and feces, and iii) conventionally scraped manure. From the results of these studies, NH_3 emission from post-separation storage of realistically separated urine and feces within the first seven days was greater than that from the storages of the idealistically separated urine and feces. However, the idealistically separated urine eventually and rapidly lost NH_3 in the next two weeks resulting in higher NH_3 losses than that from storage of the realistically separated urine and feces by the end of the week 3. Based on these studies, therefore, it is evident that avoiding the contact of urine and feces would not necessarily result in more mitigation of NH_3 emissions. It appears that the effort of avoiding absolute contact of urine and feces will just delay the initiation of NH_3 loss by only a few days. This study thus suggested that the conventional method of scraping of urine and feces from barn would be a better strategy for reducing NH_3 emissions from post-collection storages compared to the urine-feces separation approaches.

Part-II: Emissions Modeling

Study 1. A Model for K_{oL} of NH_3

In this study, the K_{oL} of NH_3 from dilute dairy manure slurries was modeled empirically in a laboratory convective emission chamber (CEC). Air temperatures (T_{air}), liquid temperatures (T_L), air velocities (V_{air}), and total solids (TS) concentration usually experienced in Pacific Northwest were the respective factors included in this empirical model. The K_{oL} increased with increase in liquid temperature between 5 and 35°C. The K_{oL} increased with increase in air velocity within the air velocity range examined in this study (0.5 to 4.0 m/s: which implies NH_3 loss increases with increasing air or wind velocity. The K_{oL} decreased with increase in air temperature within 15-35°C temperature range. Since ambient air and liquid manure temperatures move in the same direction, these two parameters counteract the effect of each other. The increase in NH_3 loss due to increasing liquid temperature is moderated by decrease in NH_3 loss attributed to the simultaneously increasing ambient air temperature. The K_{oL} decreased with increase in the concentrations of TS in the range of 0.5 to 2.5%; suggesting that solids inhibit the mass transfer coefficient of NH_3 from liquid dairy manure. The higher the concentration of TS the higher was the inhibition and the lower was the NH_3 loss. The developed model for predicting the K_{oL} of NH_3 from liquid dairy manure exhibited an NME of 9.6%; demonstrating good fit with the experimental data. The sensitivity of K_{oL} to all four model parameters was observed to be as follow, in descending order: liquid manure temperature, ambient air temperature, wind or air velocity, and total solids concentrations, respectively.

Study 2. A model for K_d of NH_4^+

In this part of the study, ammonium ion (NH_4^+) dissociation constant (K_d) was empirically modeled at a pH of 9; at four temperatures (5, 15, 25, and 35°C) generally experienced in the US Pacific Northwest, and five TS concentrations (0.5, 1.0, 1.5, 2.0, and 2.5%; w/w) common in flushed-dairy manure. When the effect of temperature was considered alone, the K_d of NH_4^+ increased with increase in temperature. From 5 to 35°C, the K_ds increased by approximately 1.6 times for every 10°C rise in temperature. This indicates that the increase in temperature results in more fraction of unionized NH_3 which can in turn result in increased NH_3 emissions into the surroundings. The K_d of NH_4^+ decreased linearly with the concentration of TS indicating an increasing inhibition of NH_4^+ dissociation with increasing TS level in liquid dairy manure. The empirical model developed for K_d of NH_4^+ as a function of temperature and the concentration of TS had an R^2 value of 0.97 indicating that the model was strongly consistent with the experimental data. This model is, therefore, reliable for determination of the K_d of NH_4^+ in liquid dairy manure within the experimental conditions covered in this study (i.e. in the range 0.5 to 2.5% TS concentrations, and in the temperature range of 5 to 35°C).

Study 3. Process Model Validation

A process-based model was developed to quantify NH_3 emissions from dilute dairy manure via incorporation of the two developed empirical sub-models (see the preceding studies 1 and 2) of: the overall mass transfer coefficient (K_{oL}) of NH_3 from liquid dairy manure; and the dissociation constant (K_d) of ammonium ion (NH_4^+) in liquid dairy manure. The model predictions were validated with directly measured NH_3 emissions from a full-size dairy wastewater lagoon. The measured NH_3 fluxes increased linearly with increase in the day's temperature and ranged from 19.97-41.1 $\mu g/m^2/s$. The corresponding predicted emissions increased from 25.7-35.2 $\mu g/m^2/s$. The normalized mean error (NME) between the model-predicted values and the measured values was 15%. The sensitivity analyses showed that the emission fluxes are directly proportional to the lagoon liquid temperature and air velocity. The fluxes, on the other hand, were inversely proportional to both total solids concentrations and air temperature. The effective sensitivity of the model to both liquid temperature and wind velocity was, however, higher than the effective sensitivity of the model to both the TS concentrations and air temperature; within the ranges of these respective parameters in this study.

Recommended Future Work:

1. In order to initiate NH_3 emissions mitigation strategies based on the effects of solids and/or ionic strength on the K_d of NH_4^+ in dairy manure, it important to conduct further studies to delineate the effects of solids from those of ionic strength.
2. The NH_3 emissions process model developed in this study needs to be rigorously validated with data collected over longer periods of times at geographically different dairy waste anaerobic lagoons within the Pacific Northwest.
3. A user friendly computer-interface to promote wide adoption of the model developed in this work to all stake holders is the natural next stage.
4. It is also important to use the approach outlined in this work to determine the effect of common animal manure treatment technologies (anaerobic digestion, aerobic digestion, etc.) on the ammonia mass transfer coefficient and the dissociation constant in order to understand potential negative or positive impacts on ammonia emissions during post-treatment storages.