Review: Ammonia emissions from dairy farms and beef feedlots[1]

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USA; [3]USDA-Agricultural Research Service-Conservation and Production Research Laboratory, Bushland, TX,
USA; [4]Agriculture and Agri-Food Canada, Lethbridge Research Centre, Lethbridge, Alberta, Canada T1J 4B1;
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Hristov, A. N., Hanigan, M., Cole, A., Todd, R., McAllister T. A., Ndegwa, P. and Rotz, A. 2011. **Review: Ammonia emissions from dairy farms and beef feedlots**. Can. J. Anim. Sci. **91**: 1–35. Ammonia emitted from animal feeding operations is an environmental and human health hazard, contributing to eutrophication of surface waters and nitrate contamination of ground waters, soil acidity, and fine particulate matter formation. It may also contribute to global warming through nitrous oxide formation. Along with these societal concerns, ammonia emission is a net loss of manure fertilizer value to the producer. A significant portion of cattle manure nitrogen, primarily from urinary urea, is converted to ammonium and eventually lost to the atmosphere as ammonia. Determining ammonia emissions from cattle operations is complicated by the multifaceted nature of the factors regulating ammonia volatilization, such as manure management, ambient temperature, wind speed, and manure composition and pH. Approaches to quantify ammonia emissions include micrometeorological methods, mass balance accounting and enclosures. Each method has its advantages, disadvantages and appropriate application. It is also of interest to determine the ammonia emitting potential of manure (AEP) independent of environmental factors. The ratio of nitrogen to non-volatile minerals (phosphorus, potassium, ash) or nitrogen isotopes ratio in manure has been suggested as a useful indicator of AEP. Existing data on ammonia emission factors and flux rates are extremely variable. For dairy farms, emission factors from 0.82 to 250 g ammonia per cow per day have been reported, with an average of 59 g per cow per day ($n = 31$). Ammonia flux rates for dairy farms averaged 1.03 g m^{-2} h^{-1} ($n = 24$). Ammonia losses are significantly greater from beef feedlots, where emission factors average 119 g per animal per day ($n = 9$) with values as high as 280 g per animal per day. Ammonia flux rate for beef feedlots averaged 0.174 g m^{-2} h^{-1} ($n = 12$). Using nitrogen mass balance approaches, daily ammonia nitrogen losses of 25 to 50% of the nitrogen excreted in manure have been estimated for dairy cows and feedlot cattle. Practices to mitigate ammonia emissions include reducing excreted N (particularly urinary N), acidifying ammonia sources, or binding ammonium to a substrate. Reducing crude protein concentration in cattle diets and ruminal protein degradability are powerful tools for reducing N excretion, AEP, and whole-farm ammonia emissions. Reducing dietary protein can also benefit the producer by reducing feed cost. These interventions, however, have to be balanced with the risk of lost production. Manure treatment techniques that reduce volatile N species (e.g., urease inhibition, pH reduction, nitrification-denitrification) are also effective for mitigating ammonia emissions. Another option for reducing ammonia emissions is capture and treatment of released ammonia. Examples in the latter category include biofilters, permeable and impermeable covers, and manure incorporation into the soil for crop or pasture production. Process-level simulation of ammonia formation and emission provides a useful tool for estimating emissions over a wide range of production practices and evaluating the potential benefits of mitigation strategies. Reducing ammonia emissions from dairy and beef cattle operations is critical to achieving environmentally sustainable animal production that will benefit producers and society at large.

**Key words:** Ammonia emission, manure, mitigation, dairy cow, beef cattle

Abbreviations: AFO, animal feeding operations; **AU**, animal unit (for measuring emissions); **BLS**, backward Lagrangian stochastic; **CP**, crude protein; **DGS**, distillers' grains with or without solubles; **DM**, dry matter; **FG**, flux gradient; **FTIR**, Fourier transform infrared; **GHG**, greenhouse gas; **LU**, livestock unit (for measuring emissions); **MM**, micrometeorological methods; **MNE**, efficiency of transfer of feed N into milk protein N; **NSS**, non-steady state; **OEB**, ruminal N balance in the Dutch reporting system; **PM$_{2.5}$**, fine particulate matter; **RDP**, ruminally degradable protein; **SS**, steady state; **TAN**, total ammonial N; **USEPA**, United States Environmental Protection Agency

Hristov, A. N., Hanigan, M., Cole, A., Todd, R., McAllister T. A., Ndegwa, P. et Rotz, A. 2011. **Émissions d'ammoniac des élevages de bovins laitiers et de boucherie: tour d'horizon**. Can. J. Anim. Sci. **91**: 1–35. L'ammoniac qu'émettent les élevages pose un problème à la fois pour l'environnement et la santé, car il concourt à l'eutrophisation des eaux superficielles et contamine les eaux souterraines en nitrates, acidifie le sol et engendre la formation de particules fines. Il peut aussi aggraver le réchauffement climatique par la création d'oxyde nitreux. Outre ces préoccupations d'ordre sociétal, les émissions d'ammoniac entraînent une diminution du pouvoir fertilisant du fumier, ce qui constitue une perte nette pour l'agriculteur. Une importante partie de l'azote présent dans le fumier des bovins, essentiellement sous forme de l'urée que contient l'urine, se transforme en ammonium avant de s'évaporer dans l'air en tant qu'ammoniac. Les émissions d'ammoniac des élevages sont difficiles à calculer en raison des facteurs de diverse nature qui régulent la volatilisation du gaz, notamment la gestion du fumier, la température ambiante, la vitesse du vent, ainsi que la composition et le pH des déjections des animaux. Parmi les stratégies employées pour les quantifier figurent des méthodes micrométéorologiques, celle du bilan massique et celle des enceintes. Chacune a ses avantages et ses inconvénients, et s'applique différemment. Il est également intéressant de connaître le potentiel d'émission d'ammoniac (PEA) du fumier, indépendamment des paramètres environnementaux. D'aucuns suggèrent de recourir au rapport entre l'azote et les minéraux non volatils (phosphore, potassium, cendres), ou au ratio des isotopes d'azote dans le fumier. Les données existantes sur les coefficients et le flux des émissions d'ammoniac varient considérablement. Pour les exploitations laitières, on rapporte des coefficients d'émission de 0,82 à 250 g d'ammoniac par vache et par jour, avec une moyenne de 59 g par animal quotidiennement ($n = 31$). Les flux d'ammoniac des exploitations laitières s'établissent en moyenne à 1,03 g par m^2 à l'heure ($n = 24$). Les pertes d'ammoniac sont sensiblement plus élevées dans les élevages de bovins de boucherie, où les émissions atteignent en moyenne 119 g par animal et par jour ($n = 9$), avec un maximum allant jusqu'à 280 g par sujet quotidiennement. Dans les élevages de bovins de boucherie, les flux d'ammoniac se situent en moyenne à 0,174 g par m^2 à l'heure ($n = 12$). Quand on recourt au bilan massique de l'azote, on estime que les pertes quotidiennes d'azote sous forme d'ammoniac se situent entre 25 et 50% de l'azote excrété dans le fumier des vaches laitières et des bovins de boucherie. Parmi les moyens visant à atténuer les émissions d'ammoniac, on retrouve la réduction du N excrété (surtout dans l'urine), l'acidification des sources d'ammoniac et la liaison de l'ammonium à un substrat. Réduire la concentration de protéines brutes dans la ration des animaux et la dégradation des protéines dans le rumen sont de puissants outils pour diminuer l'excrétion du N, le PEA et les émissions globales d'ammoniac de l'exploitation. En baissant la concentration de protéines dans la ration, le producteur épargnera aussi sur le coût des aliments. De telles interventions doivent cependant être soupesées avec le risque d'une baisse de production. Les techniques de conditionnement du fumier qui réduisent les formes volatiles de l'azote (par ex., inhibition de l'uréase, diminution du pH, nitrification-dénitrification) atténuent aussi efficacement les émissions d'ammoniac. Une autre solution serait de capter et de traiter les émissions, notamment au moyen de filtres biologiques, avec des membranes perméables et imperméables ou par l'incorporation au sol, pour la production de cultures ou de pâturages. La simulation de la formation et de la volatilisation de l'ammoniac au niveau des procédés est un instrument utile pour estimer les émissions d'un vaste assortiment de méthodes de production, ainsi que pour évaluer les avantages éventuels des stratégies d'atténuation. Il est capital qu'on arrive à diminuer les émissions d'ammoniac venant des élevages de bovins laitiers et de boucherie si l'on garantir la pérennité des productions animales sur le plan environnemental, et faire en sorte que les agriculteurs comme la société en général en bénéficient.

Mots clés: Émissions d'ammoniac, fumier, vaches laitières, bovins de boucherie

Ammonia (NH_3) emitted from animal feeding operations (AFO) is a major air and water pollutant contributing to eutrophication, soil acidity, and aerosol formation that can impair atmospheric visibility and human health [United States Environmental Protection Agency (USEPA) 2004a]. As a result, the USEPA ruled on 2009 Jan. 20, that AFO that did not endorse the 2005 USEPA Air Quality Compliance Agreement must notify emergency response officials, if they emit 45 kg or more of NH_3 or hydrogen sulfide in a 24-h period (USEPA 2009a). Animal feeding operations are exempt from reporting under the Comprehensive Environmental Response, Compensation, and Liability Act only for emissions from normal manure handling on farms; reporting is mandatory for other forms of release, such as from burst anhydrous NH_3 tank, breached lagoon or holding pond, or manure spills. Thus, it becomes critical for the animal industries to understand the factors controlling and make every effort to reduce NH_3 emissions from animal operations.

Perhaps one of the least understood processes to which NH_3 emitted from livestock operations is contributing is atmospheric fine particulate matter formation. The process of NH_3 formation and volatilization from animal manure is almost instantaneous and begins immediately after urine and feces are excreted. Once emitted into the atmosphere, NH_3 enters rapidly into simple chemical reactions primarily with sulfur and nitrogen (N) oxides. The dynamics of these reactions, however, are very complex and depend on environmental conditions and concentration of reactants. For an excellent review of atmospheric NH_3 chemistry the reader is referred to Renard et al. (2004). In general, NH_3 is present in the troposphere in very low concentrations, ranging from 1 to 25 ppb (Renard et al. 2004). Due to its high reactivity, NH_3 reacts with atmospheric acids such as sulfuric and nitric (Fig. 1) forming ammonium sulfate, ammonium bisulfate or ammonium nitrate, considered $PM_{2.5}$ (particles with aerodynamic diameter less than or equal to 2.5 µm; sometimes

$SO_2 \longrightarrow H_2SO_4$

$NO_2 \longrightarrow HNO_3$

Ammonia

$(NH_4)_2SO_4$ or $(NH_4)HSO_4$

NH_4NO_3
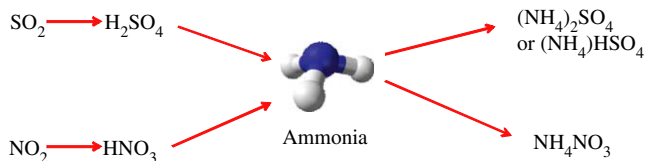
Fig. 1. A simplified diagram representing the main atmospheric reactions leading to formation of fine particulate matter ($PM_{2.5}$) from ammonia.

referred to as "fine particles"; USEPA 2004b). These particles contribute to air pollution, which globally is estimated to cause up to 2 million premature deaths annually (WHO 2005). Of the pollutants monitored by the World Health Organization, particulate matter affects more people than any other air pollutant. Even low concentrations of air pollutants have been related to a range of adverse health effects (Oberdorster 2000; Miller et al. 2007). Fine particulate matter ($PM_{2.5}$) is considered among the most dangerous as, when inhaled, it may reach the peripheral regions of the bronchioles and interfere with gas exchange inside the lungs (WHO 2005).

As farm animals are considered the greatest contributor to gaseous NH_3 emissions [50% of NH_3 emissions in the United States; National Research Council (NRC) 2003], it is important to quantify their contribution to $PM_{2.5}$. Assuming that NH_3 contribution to $PM_{2.5}$ is through formation of ammonium nitrate and ammonium sulfate (USEPA 2004b) and that sulfuric acid is rapidly converted to sulfate and is usually not present as free acid in the atmosphere (USEPA 2004b; Wexler and Johnston 2008), this contribution can be estimated based on data from the National Air Quality Status and Trends Report (USEPA 2008). Across different regions and weather conditions, $PM_{2.5}$ attributable to NH_3 emitted from livestock operations averaged 5 to 11% (Hristov 2011). Under certain climatic conditions, the estimated contribution of farm animals to atmospheric $PM_{2.5}$ concentration may be significant in certain areas of the US (up to 20% for the North Central region in cool weather).

Ammonia emitted from livestock operations can directly contribute to water eutrophication. Atmospheric transport and fate of NH_3 depend on meteorological chemical conditions (Wu et al. 2008). Models have predicted an average lifetime of atmospheric NH_3 aerosol of 3 to 4 d and a ratio of wet to dry deposition of about 6 to 7 (Pye et al. 2009). Ammonia conversion to ammonium is also dependent on climatic conditions. Wu et al. (2008) estimated that from 10 to 40% (summer) and 20 to 50% (winter) of emitted NH_3 can be converted to ammonium near source, and 40 to 100% (summer) and 50 to 98% (winter) downwind. Thus, NH_3 emitted from animal operations may impact water quality immediately or at a considerable distance from the emission source. For example, Grimm and Lynch

(2005) estimated ammonium wet deposition in the Chesapeake Bay watershed at 2.6 kg ha^{-1}, or about 47% of the total inorganic N deposition.

Although ammonia is not a greenhouse gas (GHG), it may indirectly contribute to agricultural emissions of nitrous oxide (N_2O), a potent GHG with a global warming potential of approximately 300 times that of CO_2. Agricultural N_2O emissions are primarily soil emissions due to microbial processes of nitrification and denitrification (USEPA 2010). Nitrogen added to soil (as fertilizer or manure) can directly or indirectly contribute to N_2O emissions. Ammonia volatilized from manure, for example, can be re-deposited on soil and eventually converted into N_2O. Nitrate in leachate and soil run-off can be converted into N_2O through aquatic denitrification (USEPA 2010). According to some estimates, manure (grazing animal and managed manure) constitutes about 17% (or 6.7 Tg of N) of the N_2O sources in the United States (Del Grosso et al. 2008). Thus, N and NH_3 volatilization from manure can directly contribute to GHG emissions from animal agriculture.

NITROGEN METABOLISM IN THE RUMINANT ANIMAL

Several aspects of ruminant nutrition can be related directly to NH_3 emissions from cattle manure: (1) inefficient utilization of feed N in the rumen; (2) inaccurate prediction of the animal degradable and undegradable protein requirements, leading to overfeeding of dietary N; and (3) underestimation of the role of urea recycling to the rumen as a mechanism of N preservation.

Nitrogen metabolism in ruminants is a more complex process than in monogastric animals because of extensive breakdown and modification of proteins in the reticulo-rumen. The ruminant animal is unique in its ability to convert feed N into microbial protein. The metabolizable protein needs of the ruminant are met primarily from two sources of amino acids: microbial protein synthesized in the rumen and feed protein undegraded in the rumen, with a small contribution from endogenous protein secretion (NRC 2001). A portion of the protein flow from the rumen is derived from endogenous protein secreted into the rumen, but since this is derived from previously absorbed protein, it is not considered to provide a net contribution to the animals' amino acid requirement. Feeding inadequate amounts of protein that can be degraded by the microbes in the rumen and used to synthesize microbial protein can compromise microbial growth, and inadequate flow of both feed and microbial protein to the small intestine can compromise animal performance. However, overfeeding either the microbes or the animal will result in catabolism of the protein or amino acids, conversion of the excess N to urea, and excretion of urea in urine. Thus, from an environmental point of view, it

is important to match dietary protein supplies as closely as possible to microbial and animal needs.

A large portion of the dietary proteins and non-protein compounds entering the rumen are degraded by the ruminal microorganisms to peptides, amino acids, and eventually to NH_3 (Hristov and Jouany 2005). These compounds are used by the microbes to synthesize protein. Ammonia is also absorbed into the blood stream, through the rumen wall or other sections of the gastrointestinal tract (Reynolds and Kristensen 2008) where it is cleared by the liver and converted to urea. Microbial protein has amino acid composition very similar to the amino acid composition of tissue and milk protein (NRC 2001; Lapierre et al. 2006), which makes it almost an ideal source of amino acids for the animal. Microbial and feed proteins that by-pass ruminal degradation, however, may not provide digestible essential amino acids in quantities and ratios sufficient for maintenance or production needs. Even if the amino acids absorbed in the gut closely match the amino acid requirements, the liver significantly modifies the amino acid profile of metabolizable protein (Blouin et al. 2002; Hanigan 2005) and catabolizes amino acids that are in excess of needs. Metabolized amino acids are deaminated and the resulting NH_3, being a neurological toxin, is converted to urea by the liver and subsequently released into blood. Blood urea is excreted by the kidneys or recycled back to the digestive tract (Lapierre and Lobley 2001; Stewart and Smith 2005), contributing to the ruminal and large intestinal NH_3-N pools.

Urea recycling to the digestive tract of the ruminant animal is an important N preservation mechanism. In spite of intensive research in the past couple of decades, however, the processes controlling urea recycling are not completely understood, although ruminal NH_3 concentrations and plasma urea-N concentrations appear to be important factors (Reynolds and Kristensen 2008). Recent studies have re-emphasized the importance of urea recycling in preserving N and in providing available N for microbial growth when dietary protein is deficient (Lapierre and Lobley 2001; Reynolds and Kristensen 2008). The level of dietary crude protein (CP) is one of the most important factors determining urea recycling rate to the gut and utilization by the microbes in the rumen (Reynolds and Kristensen 2008). A series of classic experiments from the Research Center for Animal Production in Dummerstorf-Rostock have demonstrated, for example, that the efficiency of supplemental urea utilization for microbial protein synthesis in the rumen is sharply decreased (respectively, urinary N losses are increased) as dietary or plant protein availability increases (Voigt et al. 1984; Piatkowski and Voigt 1986). Growing cattle (Wickersham 2008a, b), or dairy cows (Ruiz et al. 2002) fed low-CP diets have the ability to recycle to the gut virtually all urea synthesized in the liver, with very little being lost in urine. Urea transferred to the gastrointestinal tract will be utilized for anabolic purposes, i.e., microbial protein synthesis, at a much greater rate in ruminants fed low-CP diets (Reynolds and Kristensen 2008). Even at high levels of dietary CP intake, cattle recycle a significant proportion of urea to the gut, but its efficiency of utilization is low (Gozho et al. 2008).

Current feeding systems for ruminants in the United States (NRC 1996, 2001) do not account for urea recycling, and likely overestimate the protein (particularly ruminally degradable protein, RDP) requirements of the animal. Meta-analysis of a large dataset (1734 diets) demonstrated that among several dietary and animal performance variables, dietary CP was the most important factor determining milk N efficiency in dairy cows (Huhtanen and Hristov 2009). Variability in milk yield may explain some of the variability in milk N efficiency when included in a model with dietary CP, but was insignificant as a stand-alone prediction variable. Hristov and Huhtanen (2008) estimated that increasing dietary CP concentration 1 percentage unit may increase milk protein N yield by approximately 2.8 g d^{-1}, but will result in 35.7 g d^{-1} of dietary N not being utilized for milk protein synthesis. A major fraction of this unaccounted N will be excreted as urea in urine. This has important implications as urinary N is more susceptible to leaching and volatile losses than fecal N (Bussink and Oenema 1998). For example, Huhtanen et al. (2008), using a dataset of mainly grass silage-based diets, estimated that 84% of the incremental N intake at constant dry matter (DM) intake is excreted in urine. Therefore, restricting N intake is an obvious way to achieve an improvement in the efficiency of N utilization by ruminants and to limit the excretion of nitrogenous compounds into the environment.

MECHANICS OF AMMONIA FORMATION AND VOLATILIZATION

Urea is the main nitrogenous constituent of ruminant urine. Bristow et al. (1992), among others, reported that urea N represented from about 60 to 90% of all urinary N in cattle, with similar proportions for sheep and goats. Other significant nitrogenous compounds were hippuric acid, creatinine, and metabolites of purine bases catabolism, such as allantoin, uric acid, xanthine, and hypoxanthine. Bussink and Oenema (1998) summarized existing literature and reported that urinary urea, as proportion of total N, ranged from 50 to 90%. In the urine of high-producing dairy cows, urea represents 60 to 80% or more of total urinary N (Reynal and Broderick 2005; Vander Pol et al. 2007) and proportionally increases as dietary CP level and intake increase (Olmos Colmenero and Broderick 2006). Urea is the main source of NH_3 volatilized from cattle manure (Bussink and Oenema 1998). These authors indicated that 4 to 41% of the urinary N may be volatilized, while N volatilization from feces is considerably less at 1 to 13%. Under simulated feedlot conditions, Stewart (1970) reported that 25 to 90% of urinary N was lost

as NH_3 within 48 h of excretion. In a 1-yr study at two Texas feedlots, Cole and Todd (2009) noted that N volatilization losses ranged from 64 to 124% of urinary N excretion, with an average of 79%. Urea is not volatile, but once it comes in contact with feces it is rapidly hydrolyzed to NH_3 and carbon dioxide by the abundant urease activity in fecal matter (Bussink and Oenema 1998). Lee et al. (2009) showed very low ammonium concentration in fresh manure, but a rapid hydrolysis of urea in urine resulting in a sharp increase in ammonium concentration in manure and NH_3 volatilization rates. In this study, concentrations of urea in manure decreased from 3.7 to 0.7 mg mL^{-1} in 24 h, representing an 80% loss of urea. Such a loss equates to an approximate loss rate of 7% h^{-1}, which is much less than was observed by Hollmann et al. (2008) in a flush barn. However, the estimates of Hollmann et al. (2008) would have included some loss of NH_3 from the water used to flush the barn, a factor that may explain the differences in emission rates between these studies. James et al. (1999) observed that essentially all of the urea present in manure was converted to NH_3 and volatilized within 26 h after excretion. Using a feedlot pen surface, Cole et al. (2009a, b) noted that the chemical composition of fresh urine spots differed from drier areas of the pen and that NH_4^+ concentrations in the pen surface increased 10-fold within 5 min of urine application, then decreased by approximately 50% over the next 2 h. Surface pH also increased rapidly. Nitrogen concentration and surface pH returned to background levels after 4 d. These changes in the pen surface chemistry agree well with NH_3 flux data from urine spots. Using surface isolation flux chambers, Rhoades et al. (2005) reported that NH_3 emissions from urine spots were 10 to 20 times the emissions from dry pen surfaces. Similarly, using a wind tunnel, Petersen et al. (1998) noted that NH_3 loss from fecal pats in pastures was negligible, whereas losses from urine ranged from 2 to 52% of urinary N.

Lee and Hristov (2010a) quantified the relative contributions of urinary N and fecal N to NH_3-N volatilization losses from cattle manure. Feces and urine from lactating dairy cows were labeled separately with ^{15}N, combined in a 1:1 ratio, and incubated for 10 d in a laboratory-scale closed-chamber system. The proportion of NH_3-N originating from fecal N (Fig. 2a) was negligible in the first 48 h of the incubation and gradually increased to 11% of the emitted NH_3-N as mineralization of fecal N progressed. The proportion of NH_3-N originating from urinary N was 94% at 24 h, decreasing gradually to 87% over the 10-d incubation (Fig. 2b). This study clearly identified urinary N as the principal source of NH_3-N volatilized from cattle manure during the initial 10 d of storage, accounting for an average of 90% of the emitted NH_3-N. Using a similar approach, Thomsen (2000) estimated that urinary N accounted for 79% of the total N losses from sheep manure after 7 d of composting, decreasing to

64% at the end of the 86-d storage period. In manure stored anaerobically, urinary N accounted for 94% of the total N losses after 28 d and for 68% at 86 d.

The complete hydrolysis of urea to NH_3 (or NH_4^+) in aqueous environments is catalyzed by the enzyme urease, with nickel as a co-factor in the urease active sites, and occurs in two steps (Todd and Hausinger 1989; Kaminskaia and Kostic 1997; Udert et al. 2003). In the first step (Eq. 1), 1 mole of urea is hydrolyzed into 1 mole of NH_3 and 1 mole of unstable carbamic acid. Carbamic acid then spontaneously decomposes into a second mole of NH_3 and 1 mole of CO_2 (Eq. 2). Effectively, a mole of urea produces 2 moles of NH_3. There are no documented cases of uncatalyzed hydrolysis of urea in aqueous solutions (Kaminskaia and Kostic 1997), which demonstrates the importance of urease in the formation of NH_3 from urea.

$$NH_2(CO)NH_2 + H_2O \rightarrow NH_3 + NH_2(CO)OH \qquad (1)$$

$$NH_2(CO)OH \rightarrow NH_3 + CO_2 \qquad (2)$$

The conversion of organic-N (proteins, amino polysaccharides, and nucleic acids) to NH_4^+-N is mediated by enzymes produced by heterotrophic microbes (Horton et al. 1992; Zhang et al. 2007; Vavilin et al. 2008). First, extracellular enzymes (e.g., proteases, peptidases, chitinase, chitobiase, lyzosyme, ribonucleases, deoxyribonucleases, exonucleases, and endonucleases) break down organic-N polymers into monomers (amino acids, amino sugars, and nucleic acids). These monomers then enter the microbial cell and are further metabolized by intracellular enzymes (e.g., dehydrogenases, oxidases, and kinases) into NH_4^+ (Barak et al. 1990; Barraclough 1997). Some of the NH_4^+-N is assimilated into the microbial protein and nucleic acids, while the excess or surplus is released back into the bulk manure. For example, mineralization of protein N to NH_4^+-N involves: (1) the formation of intermediate amino acid N from protein N which is catalyzed by proteases and (2) hydrolysis of this amino acid N to NH_4^+-N, which is catalyzed by either amino acid dehydrogenases or amino acid oxidases (Nannipieri and Eldor 2009).

Ammonium-N (NH_4^+-N) itself is not volatile, but it is susceptible to volatilization through its surrogate species, NH_3-N. In aqueous environments, NH_4^+-N and NH_3-N exist in an equilibrium that is governed by both pH and temperature. At constant temperature, for example, the pH of manure determines the equilibrium between NH_4^+ and NH_3 (Eq. 3). Lower pH favors NH_4^+-N and hence lowers the potential for NH_3 volatilization (Fig. 3a; McCarty and Sawyer 1978). The reverse is also true: raising the pH shifts the equilibrium towards NH_3-N, thus increasing volatilization. Ammonia volatilization is directly proportional to the proportion of NH_3 in the total ammoniacal N ($TAN = NH_4^+$-$N + NH_3$-N) present in aqueous solutions such as manure slurry. The greatest increase
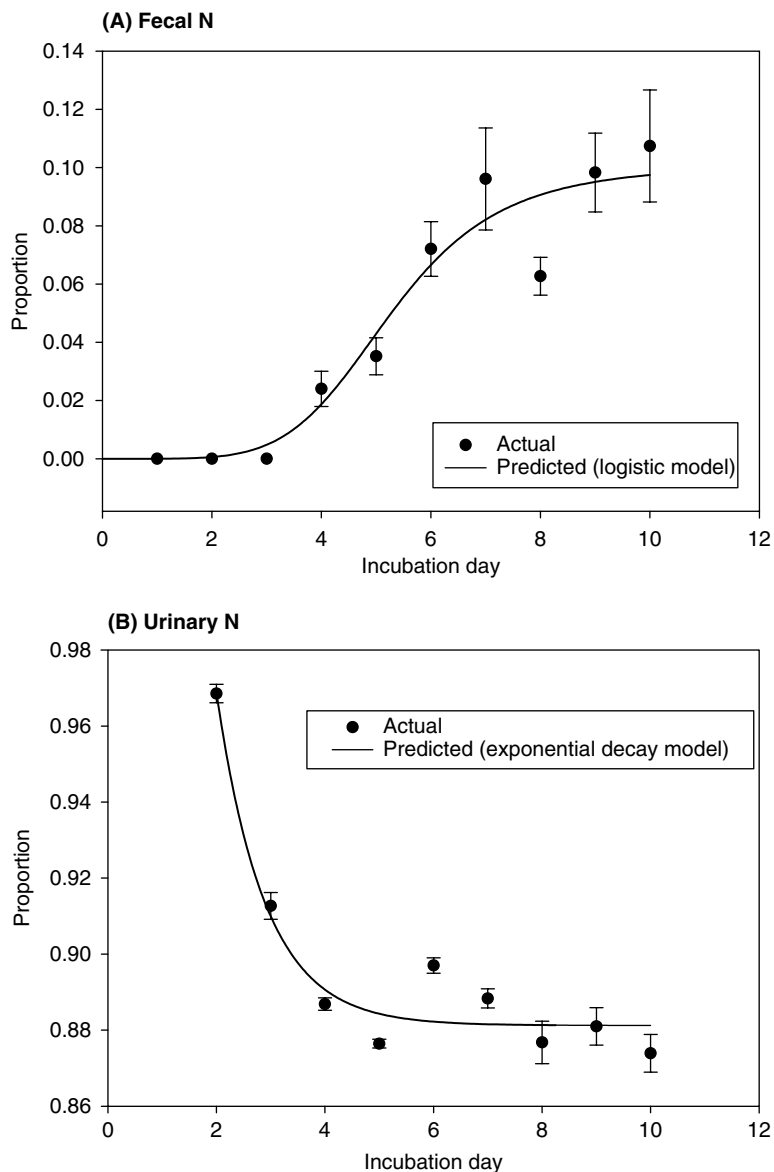
(A) Fecal N

(B) Urinary N

Fig. 2. Proportion of ammonia N originating from (A) fecal N and (B) urinary N in dairy manure incubated for 10 d in a closed-chamber system (from Lee and Hristov 2010a). Symbols are measured (means $\pm$ SE) and lines are predicted values.

in NH_3 release takes place between a pH of 7 and 10. At a pH of 7 and below, NH_3 volatilization decreases progressively such that at a pH of 4.5 there is essentially no measurable free NH_3 (McCarty and Sawyer 1978; Hartung and Phillips 1994; Ndegwa et al. 2008). The influence of temperature on NH_4^+ - NH_3 equilibrium is shown in Fig. 3b (Loehr 1974). Increasing temperature increases dissociation of NH_4^+-N to NH_3-N and thus enhances NH_3 volatilization.

$$NH_4^+ \overset{pH}{\leftrightarrow} NH_3 + H^+ \tag{3}$$

The pH at the surface of the manure, where NH_3 actually volatilizes, controls emission rate. Surface pH is

difficult to measure and model. When manure is exposed to air, dissolved CO_2 is released more rapidly than NH_3 due to a lower solubility. The rapid loss of CO_2 leads to an increase in surface pH, while the pH of the bulk of the manure remains relatively constant (Sommer et al. 2006; Montes et al. 2009). For a manure surface with constant animal movement and mixing of feces and urine such as a free stall barn floor, there is continuous mixing of the manure so the surface pH varies between the bulk pH and a value about one unit greater than the bulk pH (Montes et al. 2009). Given the sensitivity of NH_3 dissociation to pH, NH_3 concentration at the manure surface is expected to be very dynamic and variable across a manure covered floor surface.
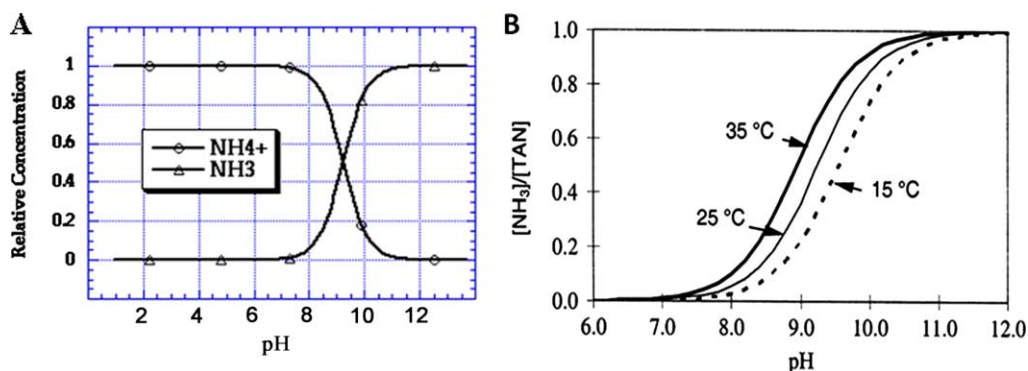
Fig. 3. Equilibrium between NH_4^+ and NH_3 in aqueous solutions as a function of pH and temperature [A: McCarty and Sawyer (1978); B: Loehr (1974)].

Generally, the process of NH_3 volatilization involves movement of NH_3 to the manure surface and subsequent release of NH_3 into the ambient air (Ni 1999; Teye and Hautala 2008). A conceptual model of NH_3 formation and volatilization is presented in Fig. 4. Transfer of NH_3 to the manure surface is achieved through diffusion, whereas the release of NH_3 from the manure surface to ambient air is mainly through convective mass transfer (van der Molen et at. 1990; Kirk and Nye 1991; Olesen and Sommer 1993; Ni 1999). In thin layers of manure, the resistance of NH_3 transfer to the surface is negligible compared with the resistance of its release into the ambient air. The latter process is thus more significant to the NH_3 volatilization process. Overall, however, NH_3 volatilization increases in response to increases in concentration of NH_4^+/NH_3 in the manure, wind speed and turbulence over the manure surface, and manure temperature and acidity (Vlek and Stumpe 1978; Olesen and Sommer 1993; Sommer et al. 1993; Teye and Hautala 2008).

QUANTIFYING AMMONIA EMISSIONS FROM ANIMAL FACILITIES

Quantifying NH_3, or any other gaseous emissions, from beef cattle feedlots and dairies entails two major challenges: 1) measuring of NH_3 concentration in the air; 2) quantifying NH_3 transfer efficiency from a surface to the atmosphere. Many methods and techniques are used to accomplish these challenges, each with advantages, disadvantages and appropriateness of use.

Instruments and techniques to measure ambient atmospheric NH_3 at open lots must be able to detect lower concentrations than those encountered in confined or housed animal production systems. For example, background NH_3 concentration typically ranges from <1 to $40 \, \mu g \, m^{-3}$ (Todd et al. 2006), with maximum NH_3 concentration in air over feedlots rarely exceeding $3000 \, \mu g \, m^{-3}$ (Todd et al. 2005). Direct methods for measuring atmospheric NH_3 fall into three broad classes: (1) chemical acid absorption, (2) optical absorption, and (3) chemical transformation (McGinn and Janzen 1998; Arogo et al. 2001; Fowler et al. 2001; Harper 2005).

Gas washing or acid scrubbing is a type of chemical acid absorption that involves actively pulling and bubbling air through an acid solution (boric, sulfuric, hydrochloric, phosphoric), where the NH_3 in the air is drawn into solution to form NH_4^+, which as a base, reacts with the acid and is chemically trapped in the solution. Subsequent laboratory analysis of the solution for NH_4^+, using photospectroscopic techniques, and knowledge of the air flow rate and duration through the acid solution allow calculation of the NH_3 concentration of the air. Gas washing is a proven, relatively inexpensive, and accurate method to measure atmospheric
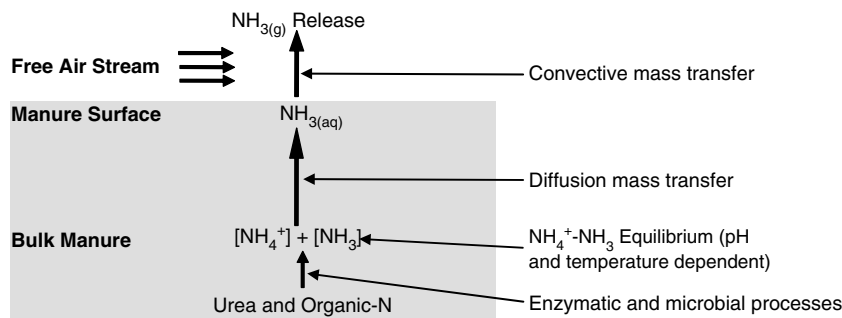

Fig. 4. A conceptual model of ammonia formation and volatilization from manure.

NH_3 in situations ranging from small plots to large feedlots (Denmead et al. 1974; Beauchamp et al. 1978; Hutchinson et al. 1982; Bussink et al. 1996; Sharpe and Harper 1997; Harper et al. 2004; Todd et al. 2006). With careful processing of samples and a sensitive laboratory analyzer, concentrations as low as $5 \mu g \, m^{-3}$ can be detected using this method. However, the process is very labor intensive and requires sample integration times on the scale of hours, which could limit applicability when finer-scaled measurements are needed. Care must be taken that the NH_3 in the air drawn through the acid scrubber does not exceed the capacity of the acid solution to react with NH_4^+.

Passive absorptive devices (Schjorring 1995; Scholtens et al. 2003; Yang et al. 2003; Sommer et al. 2004; Misselbrook et al. 2005a) trap NH_3 on dry acid-impregnated surfaces, which are subsequently extracted and sample solutions analyzed in laboratory. Passive samplers rely on wind ventilation and diffusion to convey NH_3 to the absorbing surface, so that minimum detection limits ($50-100 \mu g \, m^{-3}$) are higher than those for active gas washing or denuders. Like active gas washing, passive methods require periodic deployment and exchange of samplers, laboratory processing of samples, and hour-scale sample integration times.

Annular denuders pull air through glass tubes under laminar flow where particulates are separated, acid gases are absorbed to a basic solution coating and basic gases, like NH_3, absorbed to an acid solution coating (Harper 2005). Passive samplers and denuders, because of their relatively low cost, can be effectively used for long-term (weekly or monthly) and spatial monitoring of atmospheric NH_3 concentration (Wilson and Serre 2007; Sutton et al. 2008). However, it is important to assure that denuders recover most of the NH_3 and that the acid absorbing surface does not saturate.

Ammonia in air attenuates light at specific frequencies, and this property is used in optical instruments. Absorption in infrared wavelengths is used with the Fourier transform infrared (FTIR) method (Galle et al. 2000; Griffith and Galle 2000; Keliher et al. 2002), and in near-infrared instruments by tuned diode lasers (McGinn et al. 2003, 2007; Flesch et al. 2007; van Haarlem et al. 2008). Continuous measurement is possible, and minimum detection limits are within the range observed at feedlots. The light beam of an optical absorption instrument operates noninvasively along an open path, and gas concentration is averaged along that path, in contrast to measurements at a single point in space. Optical instrumentation is expensive and requires careful maintenance and calibration. Dust, common in feedlots, can increase the opacity of the air along the optical path and degrade an instrument's signal.

The chemiluminescence method relies on the high-temperature oxidation of NH_3 and NO_x, and NO_x only, in two separate conversions, to form NO, which is subsequently converted in the presence of ozone to NO_2. When excited NO_2 drops to a lower energy state, emitted radiation is proportional to NO concentration, and from that, NH_3 concentration can be calculated. Chemiluminescence instrumentation provides continuous monitoring of NH_3 concentration and has been used with micrometeorological methods (Phillips et al. 2004; Baek et al. 2005) and closed chambers (Baek et al. 2003; Koziel 2003).

However, the instrumentation requires line level electricity to operate and maintain an operating environment, and this requirement limits its applicability where remote operation is needed. Careful and frequent on-site calibration is also needed to maintain accuracy of measurement.

Methods to Estimate Ammonia Emissions
Ammonia volatilization is a complex biochemical and physical process. It requires an NH_3 source, a concentration gradient between the surface and the atmosphere, and the physical removal of NH_3 by atmospheric turbulence. Atmospheric turbulence is generated by the frictional retardation of the wind by the surface (mechanical turbulence) or by differential heating of the air (thermal or convective turbulence) (Thom 1975; Campbell and Norman 1998). This turbulence is manifested as swirling masses of air called eddies. In an open feedlot, turbulent transfer is usually very efficient, effectively sweeping NH_3 from the surface and maintaining the concentration gradient between surface and free air. The basic task of micrometeorological methods that estimate NH_3 emission is to describe the nature of turbulence.

Micrometeorological methods (MM) are advantageous because they do not interfere with the processes of emissions, integrate emissions over areas on the scale of entire lot, and allow continuous readings to examine temporal trends (McGinn and Janzen 1998; Fowler et al. 2001; Harper 2005). Generally speaking, MM rely on measurements in and characterization of the atmosphere near the ground. These techniques have been applied successfully to crops (Denmead et al. 1978; Harper and Sharpe 1995; Rana and Mastrorilli 1998) and natural vegetation (Denmead et al. 1974; Bussink et al. 1996; Wyers and Erisman 1998), and they are being used increasingly to characterize NH_3 emissions from beef cattle feedlots and dairies (Hutchinson et al. 1982; McGinn et al. 2003, 2007; Todd et al. 2005, 2008; Flesch et al. 2007). However, because MM typically require large, relatively homogenous land areas, replicated comparison of treatments or NH_3 mitigation strategies is often not possible (Meisinger et al. 2001; Harper 2005). Micrometeorological methods to quantify NH_3 emission can be considered in four classes: (1) direct measurement, (2) mass balance, (3) aerodynamic, and (4) complex dispersion models.

The only micrometeorological method that directly measures turbulent transfer is the eddy covariance method (Fowler et al. 2001). Eddies can be directly measured, and with a simultaneous measurement of

concentration, a direct measure of NH_3 flux determined. The method requires very rapid measurements (10 to 20 per second) of eddies and concentration. Sonic anemometers are used to measure the vertical eddies and rapid response instruments such as tunable diode lasers are used for simultaneous measurement of NH_3 levels in these eddies. The characteristic of NH_3 to readily absorb to surfaces, however, challenges the ability to accurately measure concentration with fast response instruments. Alternatively, in the relaxed eddy accumulation method, air from up-eddies and down-eddies is segregated and collected separately. After a period of accumulation, concentration is measured with slow response methods like chemiluminescence, denuders, or gas washing (McInnes and Heilman 2005; Baum and Ham 2009).

Mass balance MM account for the amount of NH_3 that passes across the upwind edge of an emitting surface and the amount that passes across the downwind edge, so that the difference is the amount emitted. The Integrated Horizontal Flux method uses profile measurements of wind speed and NH_3 to calculate the horizontal flux (the product of wind speed and concentration) at various heights (Wilson et al. 1983; Wilson and Shum 1992). The vertical flux is calculated by integrating the horizontal fluxes over the measurement heights. However, the top measurement height must be within the NH_3 plume, or there will be unaccounted NH_3 mass and flux will be underestimated. Typically, circular plots are used to simplify the determination of upwind source area (Yang et al. 2003; Todd et al. 2006), although the method can be used with strip sources (Denmead et al. 1977), irregularly shaped fields (Flesch et al. 2002; Laubach and Kelliher 2004) or finite volumes (Denmead et al. 1998). Another variant of the mass balance method is the box model. Mass balance methods assume that source strength is homogeneous, air flow is fully turbulent, and that the boundaries of the system are defined. The surface is considered the lower boundary, and the upper boundary is defined as the height where NH_3 levels equal background concentration.

The aerodynamic flux-gradient (FG) method treats turbulent flux in a manner analogous to molecular diffusion (McGinn and Janzen 1998; Fowler et al. 2001; Harper 2005). The method requires profile measurements of gas concentration, wind speed, and air temperature to calculate a FG flux estimate. The FG method assumes there is horizontal uniformity of air flow, that horizontal concentration gradients are negligible, and that vertical flux is constant with height (Thom 1975; Harper 2005) such as found at feedlots and dairies. In situations of disturbed flow these assumptions may be violated and the FG method could underestimate flux (Wilson et al. 2001). Typical of many MM, the FG method requires relatively large areas upwind of the measurements, and care must be taken to ensure that measurements are affected only be the source area of interest. Ammonia concentration

gradients can be measured with techniques such as gas washing (Hutchinson et al. 1982; Harper and Sharpe 1995; Harper et al. 2004; Todd et al. 2005), chemiluminescence (Phillips et al. 2004; Baek et al. 2005) or passive absorptive devices (Laubach and Kelliher 2004).

Complex dispersion models describe the relationship between a source of a gas and a downwind receptor or point (Harper 2005). Assumptions with regard to turbulent flow must be made to establish this relationship (Wilson et al. 2001). Sometimes, source strength of a gas is known, and a dispersion model predicts concentration at the receptor. A Gaussian plume model is an example of this type of dispersion model, in which empirical parameters describe the three-dimensional spread of a plume of gas from its source. The backward Lagrangian stochastic (BLS) model estimates flux of a gas by taking concentration of a gas measured downwind of an emitting source, and modeling the trajectories of thousands of gas particles backward to the emitting source (Flesch et al. 1995). Advantages of the BLS model include a small number of required inputs (gas concentration, wind speed and direction, atmospheric stability, defined source area). It assumes that the atmospheric surface layer is homogeneous, that flow is stationary and that the source strength is spatially uniform (Flesch and Wilson 2005), assumptions that can be challenged by the complexity of some animal feeding operations. The BLS model has been tested and compared positively to other methods for estimating fluxes of methane (Laubach and Kelliher 2005), NH_3 (Sommer et al. 2005), and with gas release experiments (Flesch et al. 1995; Gao et al. 2009), and has been successfully applied to cattle feedlots (McGinn et al. 2003, 2007; Flesch et al. 2007; Todd et al. 2008; van Haarlem et al. 2008). Harper et al. (2009) reported that BLS flux estimates from several studies ranged from -14% to $+7\%$ of known tracer releases. Gao et al. (2009), using open path lasers, found that BLS overestimated methane flux by 9% compared with known release.

Emission of nitrogenous gases can be estimated as the residual of a comprehensive N mass balance of an animal production system (Dammgen and Hutchings 2008). Several research teams (Bierman et al. 1999; Farran et al. 2006; Cole and Todd 2009) have calculated N balances for cattle feedlots. Accurate estimates of NH_3 emission using mass balance require that N contained in the stocks of rations, animals, feces, urine, removed manure, soil and runoff all be accurately accounted for; then, unaccounted N is assumed to be lost as gaseous N (see N mass balance discussion for dairy facilities in following sections). Variability in the distribution of N in stores can add to uncertainty. Since emission is estimated as the residual of this accounting, any errors in measuring or estimating the mass of N in the various stores will be propagated in the emission estimate.

Enclosure methods include chambers that completely isolate an emitting surface, and wind tunnels, that partially enclose and restrict an emitting surface. Chambers are classified as either non-steady-state (NSS) or steady-state (SS) (Rochette and Hutchinson 2005). After a NSS chamber is placed on an emitting surface, several measurements of headspace concentration are made as NH_3 accumulates over time. The emission rate is the time-dependent rate of change in concentration. In contrast, air is circulated through SS chambers at a known, constant rate, and flux rate calculated as a function of the enclosed area, flow rate, the inlet and outlet NH_3 concentration, and the molar volume of air at chamber temperature and pressure. Turnover of more than 15 chamber volumes is required to achieve optimum results; if turnover rate is too low, then flux will be a function of flow rate and normally will be generally underestimated. Care must be taken to ensure that temperature and pressure do not deviate too greatly from ambient conditions during the measurement period.

Wind tunnels partially enclose a source area, typically with open ends so that forced or natural air movement is allowed (Meisinger et al. 2001). Inlet and outlet concentration are measured along with air flow rate through the wind tunnel. Matching air flow rate with the ambient wind speed is difficult, so that wind tunnels tend to underestimate flux rate.

Chambers and wind tunnels are appropriate for comparing treatments or assessing relative emission rates, but not for quantifying actual emissions (Meisinger et al. 2001; Thompson and Meisinger 2002, 2004; Cole et al. 2007b; Paris et al. 2009; Parker et al. 2010). For example, Thompson and Meisinger (2002), appropriately used flow-through wind tunnels coupled with acid gas washing to compare NH_3 volatilization from applied dairy slurry on replicated surfaces using various incorporation methods.

Indirect Approaches in Estimating Ammonia Emissions

Ni and Heber (2008) pointed out that the three categories of NH_3 sampling methods namely; closed, point, and open path, are adequate for assessing human and animal exposure, baseline emissions, building structure and mitigation technologies, and for modeling pollutant dispersions. However, these sampling methods only cover limited sampling points or sampling paths, leaving significant uncertainties for the NH_3 concentrations at uncovered spaces. The spatial variation of NH_3 concentrations is thus still a major technical difficulty in accurate determination of NH_3 losses from feedlots and dairies. These uncertainties are reflected in the wide range of NH_3 emission data found in the literature (see also Tables 1 and 3 and related discussion).

Alternative, indirect approaches to estimate NH_3 emissions, which overcome spatial and temporal variations of NH_3 loss in AFO have been suggested. Todd et al. (2005) and Moreira and Satter (2006) proposed the

use of N:phosphorus (P) ratios in fresh and aged manure for estimating volatile N losses. As NH_3 and other nitrogenous gases (N_2, nitrous oxide, and small amounts of nitric oxide; Oenema et al. 2007) volatilize from manure, N:P ratio decreases and the decrease can be used to estimate total volatile N losses. This may also be true for other, non-volatile macro-minerals in manure [potassium (K), for example]. Unlike P, K is excreted in both feces and urine (Berry et al. 2001; Gustafson and Olsson 2004; Hristov et al. 2006b) with excess dietary K being primarily excreted in urine (Underwood and Suttle 2001). The N:P ratio technique has some limitations. For example, if significant runoff occurs it cannot be reliably used to estimate volatile N losses as P, unlike N, is primarily excreted in feces and is mostly insoluble. As runoff N would be primarily of urinary origin, the N:P ratio of runoff would be disproportionally greater than the N:P ratio of manure. In contrast, as K, similar to N, is found in both feces and urine and is preferentially excreted in urine when consumed in excess, its losses with runoff are expected to more closely simulate N losses and would likely not change N:K ratio in manure. Hristov et al. (2009) reported similarly high (but variable) NH_3 losses from a free-stall dairy barn when using N mass balance (N unaccounted in manure, milk, and body weight gain), or N:P and N:K ratios.

The relationship between manure $^{15}N{:}^{14}N$ ratio and cumulative NH_3 loss may also be useful for estimating NH_3 losses. Due to isotope fractionation, NH_3-N volatilized from manure is highly depleted in ^{15}N and the resulting manure becomes increasingly enriched in ^{15}N as NH_3 is being emitted. These relationships can be used to model and predict NH_3 losses from manure. Hristov et al. (2006a) first reported the effects of NH_3 volatilization on cattle manure $\delta^{15}N$. Similar trends were observed for hog manure (C. Kendall, personal communication) and recently reconfirmed for cattle manure (Aguerre et al. 2008; Lee et al. 2009).

It is known that animals, including ruminants, fractionate N isotopes, such that heavier isotope signatures correspond to animal waste (Steele and Daniel 1978; Hristov et al. 2009). These processes have been used to distinguish manure-derived N from indigenous soil N (Selles and Karamanos 1986; Kerley and Jarvis 1996; Kendall 1998) and manure contribution to ground- and surface-water nitrate (Karr et al. 2001; 2003). During manure storage, chemical kinetic isotope fractionation results in ^{15}N enrichment of the substrate and depletion of the product (NH_3) as lighter isotope molecules tend to react faster than molecules containing the heavier ^{15}N isotope (Mariotti et al. 1981). The isotope fractionation factor associated with NH_3 volatilization is one of the highest in the N cycle (~ 1.029, Högberg 1997), which, under favorable conditions, results in a rapid increase in ^{15}N enrichment of manure.

Lee et al. (2009) reported a rapid increase in $\delta^{15}N$ of manure N from 0.1 (day 0) to 6.7 (day 2) and 10.1‰ (day 5) (Fig. 5a). Delta ^{15}N of volatilized NH_3 increased

Table 1. Ammonia emission data from dairy barns

Reference[z]	Type of facility	Manure removal system	Ammonia emission factor [per cow (g d^{-1})]	Ammonia flux rate, per h (g m^{-2})	Method	Diet CP (% DM)	Season	Ambient temperature (°C)	Airflow
Bjorneberg et al. (2009)	Open-lot	Solid manure removal	40 250 190 150	0.03 0.17 0.13 0.10[y]	OP/FTIR spectrometer	N/E	All seasons	−8 to 9 −1 to 14 8 to 43 1 to 23	1.4 to 1.6 1.5 to 4.6 1.7 to 3.1 1.2 to 1.8 (m s^{-1})
Bluteau et al. (2009)	Tie-stall	Gutter	11.3 to 18.2[x] 5.47[w]	0.04 to 0.06[x] 0.04[w]	Ammonia mass balance	13.3	Various		17.6 to 21.4 (m^3 s^{-1})
Braam et al. (1997)	Free-stall	Scrape	12 to 36[v]	0.14 to 0.43[v]	Chemical analysis	N/E	Summer	N/E	1.7 to 2.2, (m^3 s^{-1})
Cassel et al. (2005a)	Open-lot, free-stall	Scrape, flush	34 to 115	0.03 to 1.5	Modeled & H$_3$BO$_3$ bubbler	17.6	Winter	7–18	2.1 to 3.9 (m s^{-1})
Cassel et al. (2005b)	Open-lot	Scrape, pile	50 (20 to 143)	0.01 to 0.13	Modeled & H$_3$BO$_3$ bubbler	N/E	Winter	8–15	0.5 to 5.4 (m s^{-1})
Ellis et al. (2001)	Free-stall	Scrape	3.7 to 5.9	0.33 to 0.55[u]	Dynamic chamber technique	N/E	Winter-Spring Summer	N/E	N/E
Frank et al. (2002)	N/A	N/A	N/E	0.22 to 0.60	Flux chamber	14 and 19	N/A	14	100 (m^3 m^{-2} h^{-1})
Gay et al. (2003)	Free- and tie-stall	Scrape, deep pit	N/E	0.16 (from 0.002 to 0.71)	Colorimetric detector tubes	N/E	All seasons	N/E	N/E
Hristov et al. (unpublished)	Free- and tie-stall	Gravity Scrape Flush Gutter	N/E	0.41 to 0.90 0.17 to 0.43 0.13 to 0.60 0.28 to 0.90	Photoacoustic gas monitor	>17%	Fall	8 to 16	N/E
Jarvis and Ledgard (2002)	N/E	Lagoon for the UK farm	25 (NZ) to 117 (UK)	N/E	Modeled based on literature	N/E	Annual estimates	N/A	N/A
Misselbrook et al. (1998)	Collecting yards	Scrape	13.4 1.5	0.45 0.05	Modified Lindvall hood	N/E	Summer Winter	16.5 3.9	N/A N/A
Misselbrook et al. (2000)	Various	Various	73.4 to 110.1[s]	N/E	Modeling	N/A	All seasons	N/E	N/E
Misselbrook et al. (2001)	Collecting yards	Scrape	0.19 to 1.45[r]	0.34 to 0.84	Dynamic chambers	N/E	Fall-winter	5 to 20[10]	1.5 to 7.5, (m s s^{-1})[q]
Misselbrook et al. (2006)	Various	Various	1.15 to 1.88	0.43 to 0.56	Dynamic chambers	N/E	Various	Various (5 to 28)	N/E
Monteny and Erisman (1998)	N/E	Scrape and other	5–9 to 42–45[p]	N/E	Various	N/E	Various	N/E	N/E
Mukhtar et al. (2008)	Open-lot	Scrape or pile	25.7	N/E	Flux chamber	N/E	Various	6 to 27	N/E
Mukhtar et al. (2009)	Free-stall	Flush	12.7 30.2	N/E	Flux chamber	N/E	Winter Summer	−1.0 to 16.7 25 to 35	N/A N/A
Pinder et al. (2004b)	Various	Various	65.5 (35.9 to 152)	N/E	Modeling	N/A	All seasons	N/A	N/E
Pinder et al. (2004a)	Confined	Various	33 to 200 and 17 to 200[o]	N/E	Modeling	N/A	All seasons	N/A	N/E
Powell et al. (2008a)	Tie-stall environmental chambers	Gutter, daily	16.8 to 20.5 7.8 to 8.9 5.6 to 7.4	N/E	Ammonia in exhausted air	17 to 21.2 16.1 & 17.3 15.7 & 17.2	Spring Fall Winter	17.5 21.4 8.7	0.9 (m^3 s^{-1}) 0.40 0.32
Rumburg et al. (2008)	Free-stall	Scrape	5.4 (winter) to 432 (summer)	Average 17	Tracer gas and DOAS	N/E	Summer-winter	Avarage 18	1.2 to 3.5 (m s^{-1})

Table 1 (*Continued*)

Reference[z]	Type of facility	Manure removal system	Ammonia emission factor [per cow (g d^{-1})]	Ammonia flux rate, per h (g m^{-2})	Method	Diet CP (% DM)	Season	Ambient temperature (°C)	Airflow
Smits et al. (2003)	Partial grazing	N/E	77.5 to 65.3[n]	N/E	Modeling	N/E	Summer/winter	10 to 16	0.14 to 0.27 (m s^{-1})
Snell et al. (2003)	Free-stall	Scrape	38.9 to 85.4	0.22 to 0.46	Photoacoustic gas monitor	N/A	Winter	N/E	N/E
Teye and Hautala (2008)	Free-stall barn	Scrape, daily	12.2 to 177.5[m]	0.04 to 0.58,	Ammonia sensors	N/E	Spring	Day, 25; night, 1.5	300 to 1,500 (m s^{-1})[l]
Van Duinkerken et al. (2005)	Free-stall	Slatted floor	17.0 to 65.3[k]	N/E	Tracer gas and ammonia analysis	14 to 19	N/E	10 and 15	N/E
Zhang et al. (2005a)	N/E	Various (mostly scrape)	7.5 to 47.5	N/E	Photoacoustic gas monitor	N/A	Summer-winter	14 to 22 and 2.3 to 9.0	N/E
Zhu et al. (2000)	N/E	N/E	8.4 to 37.8[j]	0.04 to 0.18[i]	Detector tubes	N/E	N/E	9 to 11	26 to 136 (m^3 s^{-1})
n=			31	24					
Average			58.8	1.03					
SD			65.0	3.41					
Range			0.82 to 250	0.03 to 17					
Extremes			0.19 and 432	0.002 and 17					

[z]In alphabetical order.
[y]Estimated from published data. Includes emissions from pens (about 93% of the total emissions) and the storage pond (about 7% of the total emissions).
[x]Summer and fall estimates.
[w]Winter months estimates.
[v]Estimated from graphical data. Building emissions.
[u]Ammonia flux in feeding areas as high as 6.1 g m^{-2} h^{-}.
[t]Two model farms studied – United Kingdom (type of facility not described) and New Zealand (pasture-based).
[s]Based on Misselbrook et al. (2000) and referenced data.
[r]Estimated from published data.
[q]Approximation based on published graphical data.
[p]Based on literature review.
[o]Tulare County, CA and Lancaster County, PA, respectively.
[n]For extensive (<12 000 kg milk ha^{-}) and intensive (>16 000 kg milk ha^{-}) farms, respectively.
[m]Estimated based on published data. Includes 40 lactating cows and 16 heifers.
[l]Approximately estimated from published data.
[k]For low and high dietary RDP (Dutch OEB), respectively.
[j]Estimated based on published data.
[i]Approximately estimated from published data.
N/E, not published or cannot be estimated due to lack of data.
N/A, not applicable.

Table 2. Ammonia concentrations ($\mu g \ m^{-3}$) measured at commercial feedlots

Reference	Months/season	Location	Mean or range
Hutchinson et al. (1982)	April–July	Colorado	290 to 1200
McGinn et al. (2003)	May	Canada	66 to 503
	July		155 to 1488
Todd et al. (2005)	Summer	Texas	90 to 890
	Winter		10 to 250
Baek et al. (2006)	Summer	Texas	908
	Winter		107
McGinn et al. (2007)	Jun.–Oct.	Canada	46 to 1730
Rhoades et al. (2008)	March	Texas	305
	August		540

quadratically, from –22.5 (day 1) to –16.5 (day 5) and –1.3‰ (day 20; Fig. 5b). Using the general Rayleigh equation, NH_3-N losses were estimated at 28%, similar to the 33% estimated based on N mass balance. The

relationship between cumulative NH_3 losses and manure $\delta^{15}N$ [-319 (SE = 260.6) + 141.9% (SE = 23.6) manure $\delta^{15}N$] was similar to the relationship observed in previous experiments with manure samples collected from commercial dairy farms: -396.5 (SE = 65.43) + 106.3‰ (SE = 8.40) manure $\delta^{15}N$ (Hristov et al. 2009). Apparently, these processes are more complicated than a simple volatilizing pool of NH_4^+ principally because of hydrolysis of urea forming new NH_4^+ and the presence of other organic N species in manure that are measured along with the residual NH_4^+. In addition, and particularly in a field setting, reaction rates and fractionation factors are influenced by pH, temperature, wind, and humidity. Even considering these complicating factors, however, the correlation between manure $\delta^{15}N$ and the cumulative NH_3 loss is remarkable, suggesting that the trend of manure $\delta^{15}N$ may be useful for estimating NH_3 losses.

Table 3. Ammonia emissions from commercial beef cattle feedlots using N mass balance or micrometeorology techniques

Reference	Season	Ammonia flux rate (g m^{-2} h^{-1})	Ammonia emission factor (g head^{-1} d^{-1})	% of N fed
Hutchinson et al. (1982)	April–July	0.061 to 0.241	50	–
James et al. (1997)	Summer	–	–	50 to 70
Bierman et al. (1999)	Summer	–	–	53 to 63
Erickson et al. (2000)	Winter/Spring	–	–	31
Erickson et al. (2000)	Summer	–	–	54
Wood et al. (2001)	–	0013 to 0.168	–	–
Harper et al. (2004)	Summer	–	–	53
Harper et al. (2004)	Winter	–	–	29
Todd et al. (2005)	Summer	0.252	–	55
Todd et al. (2005)	Winter	0.121	–	27
Todd et al. (2005)	Annual	0.130	–	41
Cole et al. (2006)	Winter/Spring	–	66 to 108	51 to 65
Baek et al. (2006)	Summer	0.220	–	–
Baek et al. (2006)	Winter	0.019	–	–
McGinn et al. (2007)	June–October	0.302	140	63
Flesch et al. (2007)	Summer/ Spring	–	150	64
Rhoades et al. (2008)	March	0.208	–	34
Rhoades et al. (2008)	August	0.258	–	42
Todd et al. (2008)	Summer	–	126	68
Todd et al. (2008)	Winter	–	68	36
Todd et al. (2008)	Annual	–	97	53
van Haarlem et al. (2008)	Fall	–	262[1]	72[1]
Staebler et al. (2009)	September	0.230 to 0.317	204 to 283	–
Todd et al. (2009)	Annual	–	82 to 149	51 to 69
Cole and Todd (unpub.)	Summer	0.230	–	50
Cole and Todd (unpub.)	Winter	0.130	–	28
Summer emissions				
n		5	3	10
Average		0.252	138.7	56.7
SD		0.032	12.1	7.6
Winter emissions				
n		3	1	5
Average		0.090	68.0	30.2
SD		0.062	–	3.6
Annualized emissions				
n		12	9	19
Average		0.174	119.4	47.6
SD		0.085	72.8	15.2

[1]20% crude protein diet.

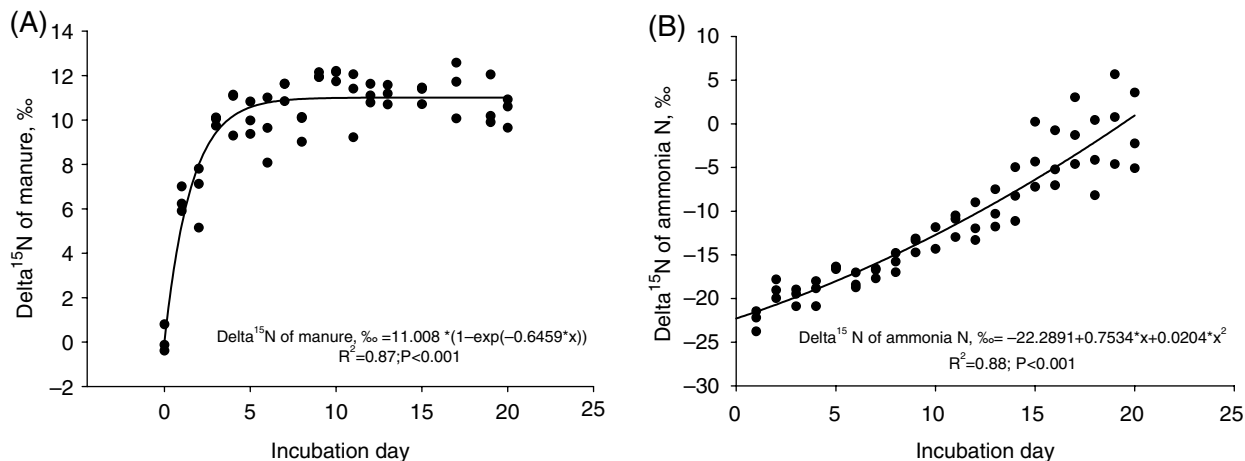**Fig. 5.** Delta ^{15}N in (A) aging manure and (B) emitted ammonia (Lee et al. 2009).

AMMONIA EMISSIONS FROM DAIRY CATTLE OPERATIONS

Earlier studies estimated that N (presumably as NH_3) losses from feed and rest alleys in free-stall dairy barns were from 0 (at, or below $-10°C$) to 50 and even 60% of the total N excreted at ambient temperatures of $20°C$ and above (Muck and Richards 1983). Hollmann et al. (2008) observed a 40% loss over a 6-h period between flushes. This study was conducted over a full year in a free-stall barn with minimal bedding in the stalls and barn flushing every 6 h with recycled water. Hristov et al. (2009) estimated that up to 50% of the N excreted from dairy cows housed in a free-stall dairy barn could not be accounted for in 24 h [i.e., Feed N intake – (N in milk + N in body weight gain)]. More recently, Hristov et al. (unpublished) (Fig. 6a) estimated that 25% of the N excreted by lactating dairy cows housed in a free-stall barn was unaccounted for in manure, milk, and body weight gain. The large difference observed between these studies may be attributed to the type of facility (Fig. 7), differences in ambient temperature during the experiments, and the manure handling systems. In the first case, the study was conducted in the summer months and the facility (Fig. 7a) had no bedding in the feeding area (where most of the feces and urine were excreted), and manure was scraped once daily. The second study was conducted in the fall, manure was scraped twice daily, and bedding (sand) and barn design (Fig. 7b) were not as conducive to large NH_3 volatilization. Using a mass balance approach with a flush system, Hollmann et al. (2008) observed a loss of 38% of the excreted N over a 6-h period during continuous deposition of manure on the barn floor, which is almost equivalent to all of the estimated urinary urea N excreted. This loss equated to an hourly loss rate of 18% of the total manure N; however, some of the loss could have occurred from the flush water as it was recycled and thus could have lost NH_3 as it transited the barn. Li et al. (2009) reported much lower rates of volatilization

from the barn floor; however, their work was performed when ambient temperatures ranged from 0 to $20°C$. Li et al. (2009) reported a significant correlation between ambient temperature and rates of volatilization. Sparks (2008) observed linear increases in rates of volatilization from scraped manure up to 25 h at which time the NH_3 volatilization rate reached a plateau. He concluded that the initial rates of volatilization were limited by low manure pH. Thus, it is possible that urea hydrolysis is rapid; however, emission of the resulting NH_3 gas may be inhibited until manure pH increases during storage (Sparks 2008).

Emissions from Various Sources in Dairy Operations

The major sources of emissions in a typical dairy operation are the barns, the manure storages (mainly anaerobic lagoons), and from field application of manure. Minor NH_3 emissions may occur from the settling ponds, sand separation basins, solid-liquid operation units, and solids composting sites. Emissions from the three major sources in a dairy (barns, lagoons, and land application) are briefly reviewed in the next paragraphs.

Emissions from Dairy Barns

Barn design, ambient temperature and ventilation, diet composition, bedding, frequency of manure removal, and manure storage can all have a dramatic effect on NH_3 emissions from dairy facilities. In the literature, NH_3 emissions from livestock operations are reported in mass per given time, on the basis of animal unit (AU) or livestock unit (LU), animal body weight, feed N intake, surface area, or volume or weight of manure. Because of this lack of uniformity in reporting standards, inter-conversion and cross-comparison of emissions from different studies is tremendously challenging. In addition, data collection periods vary widely, ranging from minutes to several months. Extrapolation of daily or
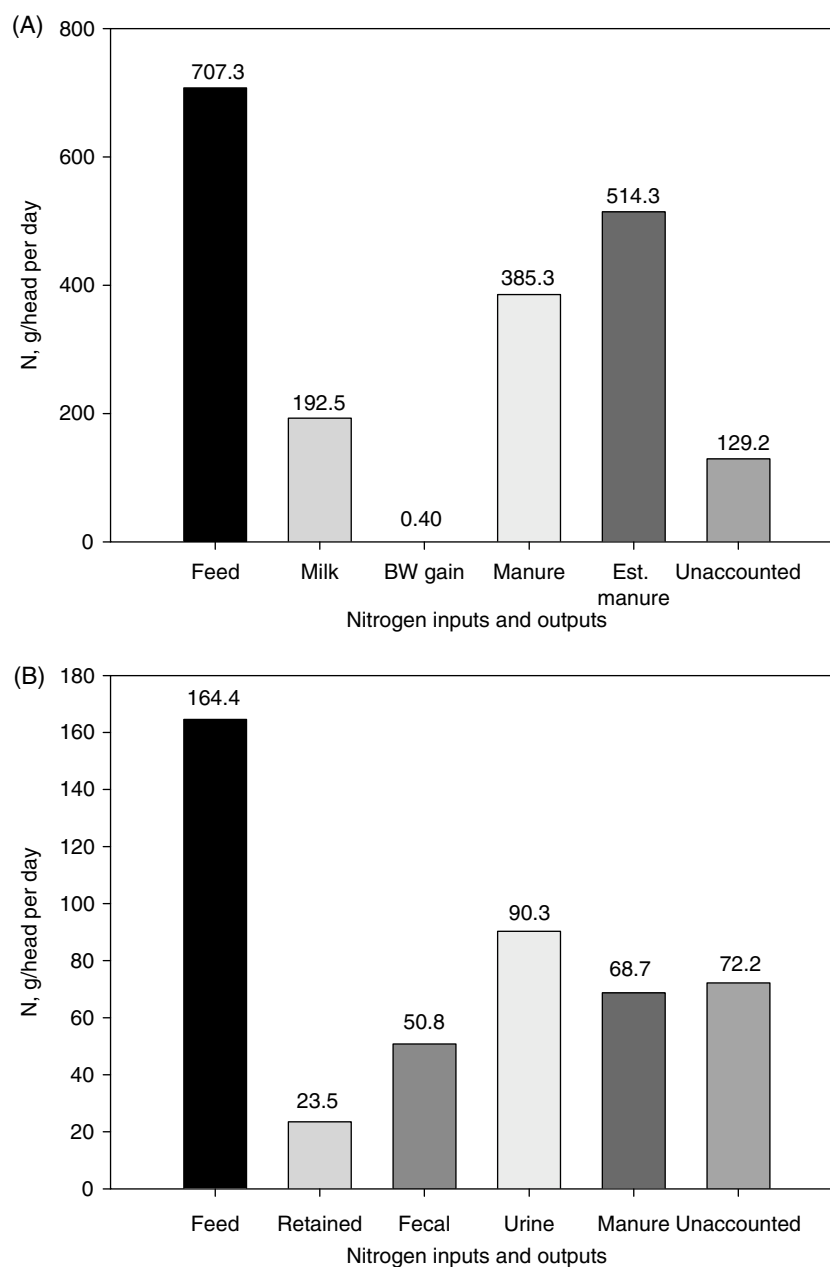
Fig. 6. Nitrogen mass balances conducted (A) at a free-stall dairy facility at Pennsylvania State University Dairy Center in Sept.–Oct. 2009 (Hristov et al., unpublished) and (B) at two commercial feedlots in the Texas panhandle over a 1-yr period (Cole and Todd 2009).

annual emissions, for example, from values obtained from a few minutes are extremely unreliable because emission rates vary widely during the day and year, in response to factors such as season, air temperature, wind speed, and humidity (Casey et al. 2006). Flesch et al. (2009) estimated that emissions from barns in three dairies in Wisconsin ranged (per animal) from 6.6 to 37 g d^{-1}. Powell et al. (2008a, b) obtained comparable results studying other dairies in Wisconsin. In a heifer tie-stall barn, emissions (per animal) ranged from 13.4

to 25.4 g d^{-1} (Powell et al. 2008a), and in a tie-stall barn for lactating cows, from 6.7 to 18.8 g d^{-1} were recorded (Powell et al. 2008b). Significantly higher emissions are reported in studies conducted in Europe. In naturally ventilated barns in Germany, emissions (per animal) in winter ranged between 38 and 85 g d^{-1} (Snell et al. 2003). Groot Koerkamp et al. (1998) recorded emissions of 24 to 48 g d^{-1} per animal in forced ventilated free-stall barns in northern Europe. In a naturally ventilated free-stall barn in the United Kingdom, emissions (per
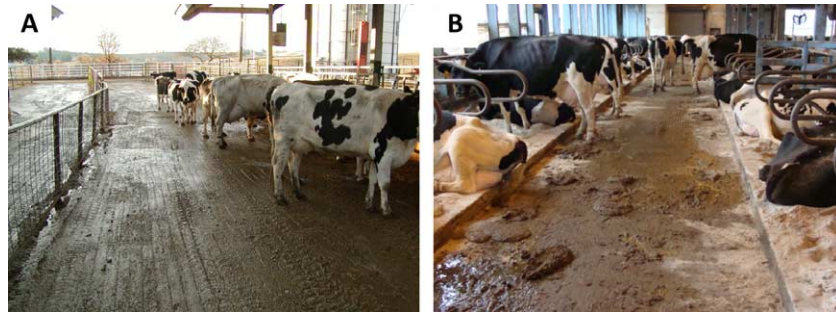
Fig. 7. Free-stall dairy facilities where the N mass balance studies were conducted [A: Hristov et al. (2009); B: Hristov et al. unpublished].

AU) were 31.6 g d^{-1} (Demmers et al. 1998). In contrast, emissions measured in Australia were much lower. Amon et al. (2001) reported emissions of 5.7 and 5.8 g d^{-1} per AU in slurry- and straw- based tie-stall barns, respectively.

Because of the complexity of factors determining NH$_3$ volatilization rates, setting average values for NH$_3$ emission from dairy barns is extremely challenging. Table 1 is summarizing the existing data on NH$_3$ emissions from dairy facilities. The individual data accurately represent emissions from facilities under specific environmental conditions, but the estimated mean NH$_3$ emission factor and flux have to be interpreted with caution. Overall, the average emission factor was calculated at 59 g d^{-1} per cow, but the values ranged from 0.82 to 250 g d^{-1}. This variability in calculated emission factors may result from true variability in emissions as well as from significant errors in emission measurements. Table 1 demonstrates the impossibility of assigning a single NH$_3$ emission factor to dairy cows across various housing, manure management, and environmental conditions. Nevertheless, it is apparent that NH$_3$ losses from dairy manure can be significant, and are expected to be greater at higher ambient temperatures and wind speed, in open-lot facilities and buildings allowing instantaneous mixing of urine and feces. Less frequent removal of manure and feeding high-CP diets are also likely to lead to greater NH$_3$ emissions (see following section).

Using a series of assumptions, in-barn NH$_3$ volatilization losses can be estimated as a proportion of manure N excreted by the cow. Average N intake can be estimated from a meta-analysis conducted by Huhtanen and Hristov (2009). The meta-analysis revealed mean CP intake of 3.9 kg d^{-1} by lactating dairy cows in North American ($n = 736$) and 3.0 kg d^{-1} per cow by those consuming northern European diets ($n = 998$), which equates to 624 and 480 g N d^{-1}, respectively (assuming N $=$ CP $\div$ 6.25). Based on the mean efficiency of transfer of feed N into milk protein N (MNE) of 24.7 and 27.7% reported for the North American and northern European datasets, respectively, average N excretions can be estimated at 470 and 347 g d^{-1}. This approach does not account for potential N retention in body weight gain, which would be minimal under normal management conditions. Calculating from these manure N excretion estimates and the mean NH$_3$ emission factor from Table 1, the proportion of manure N lost as NH$_3$ is 10 to 14%. In extreme cases, NH$_3$ losses can exceed 50% of N excreted in manure. For example, in the study by Rumburg et al. (2008), NH$_3$-N losses can be estimated as 60% of the N excreted in feces and urine: $(432 \times 0.82) \div 585$ [excreted N, g d^{-1} calculated as N intake − N in milk $\div$ 365 d $\div$ 185 cows; Table 2 in Rumburg et al. (2008)]. The Washington State University dairy (where the Rumburg study was conducted) is a typical example of a facility and feeding practices conducive to high NH$_3$ emission rates. The facility is a free-stall dairy with daily scraping of manure. The area does not produce corn or grass for silage and the only forage available from which to formulate the lactating cow diets is alfalfa (as silage or hay; Rumburg et al. 2008). As a result, dietary CP concentration is ≥19%, with most of the dietary N being soluble or RDP. As discussed in the following section, this type of diet is conducive to high urinary N losses and consequently, high volatilization rates of manure NH$_3$.

Emissions from Lagoons

Similar to the emissions from barns, it is equally challenging to establish a representative emissions factor from lagoons and other similar manure storage sytems owing to wide variations in lagoon sizes, animal diets, climate, animal numbers or density, and pre-storage processing and treatments. Nonetheless, there seems to be more uniformity in the units of measurement than with barns, because most measurements are reported per unit surface area of the lagoon per specified time interval. An overview of measured fluxes reported in the literature from several studies indicates emissions ranging from 0.13 g m^{-2} per day in winter to 15 g m^{-2} per day in summer. Rumburg et al. (2008) reported NH$_3$ fluxes ranging from 2.6 to 13.0 g m^{-2} per day from a lagoon on a research dairy farm in Washington. Smith et al. (2007) reported 3.42 g m^{-2} per day from pilot- and

farm-scale dairy slurry storage facilities in the United Kingdom. From quasi-continuous summer measurements at a dairy lagoon in Canada, McGinn et al. (2008) obtained NH_3 flux of approximately 5.1 $g\,m^{-2}$ per day. 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 $g\,m^{-2}$ per day both in winter and in summer. Flesch et al. (2009) reported seasonal emissions from a dairy lagoon in Wisconsin ranging between 2.3 and 8.7 $g\,m^{-2}$ per day in fall and summer. Zhao et al. (2007) reported emissions of 0.5 to 15 $g\,m^{-2}$ per day from a lagoon in an Ohio dairy farm over a 1-yr period, with measurements made at noon. Misselbrook et al. (2005b) reported 2.1 to 10.4 $g\,m^{-2}$ per day in a cattle farm in United Kingdom, and Sommer et al. (1993) reported emissions of 4.2 to 6.6 $g\,m^{-2}$ per day from storage of cattle slurry in Denmark.

Emissions from Land-applied Dairy Manure

Estimation of emissions factors from land application of dairy manure (or any livestock manure, for that matter) is complicated by the many variables that affect emissions. These include slurry composition, pre-storage processing and treatments, in-storage treatments, duration of storage, climatic conditions, soil conditions, and application methods. Soil water content and wind speed were the two variables that significantly influenced NH_3 volatilization from land-applied manure in studies conducted in Europe (Søgaard et al. 2002). Rumburg et al. (2006) reported NH_3 emissions (per cow) of 34 kg yr^{-1} and a flux of 47 $\mu g\,m^{-2}\,s^{-2}$ (during the first hour) from sprinkler application of dairy waste from a free-stall dairy in which manure was scraped daily and stored in a series of anaerobic lagoons that were emptied annually. Comparable NH_3 flux was reported by Thompson and Meisinger (2004), who reported approximately 56 $\mu g\,m^{-2}\,s^{-2}$ during the first 6 h following application of cattle slurry to an arable silty-loam soil. These emission fluxes are, however, significantly lower than the 110 $\mu g\,m^{-2}\,s^{-2}$ reported by Yang et al. (2003) from bovine manure slurry spread on land in Japan, determined during the first day following manure application. Research by Sommer and Olesen (2000) indicated that approximately 50% of NH_3 volatilization following land application of bovine manure slurry occurred during the first 24 h. On the other hand, Søgaard et al. (2002) successfully modeled NH_3 volatilization from land application of cattle and pig manure slurries using a Michaelis-Menten type equation with an R^2 of 0.8. Although the latter two studies suggest that NH_3 emission estimates from land application of cattle manure can be extrapolated from results of short-term (24 h or less) measurements of emissions, these approaches should be adopted with caution, given the numerous factors that govern NH_3 volatilization.

Effect of Diet on Ammonia Emissions from Dairy Cows

Available research data indicate that diets fed to animals have profound effects on NH_3 emissions from excreted manure. Overfeeding of RDP or metabolizable protein will result in excessive urinary N excretion. Feeding a diet imbalanced in amino acid supply can also result in poor feed N use efficiency because one or more amino acids can limit protein synthesis and thus the productive use of the other amino acids, resulting in increased catabolism of all amino acids. Finally, insufficient diet fermentability can limit N capture in microbial protein in the rumen, and insufficient energy supply to the animal can limit rates of protein synthesis, both of which result in poor feed N efficiency, excessive urinary N output and, consequently, increased NH_3 emissions from manure.

Generally, ruminants are relatively inefficient utilizers of dietary N. The MNE is on average 25 to 27% (Bequette et al. 2003; Huhtanen and Hristov 2009) with most of the remaining N being excreted in urine and feces. The majority of this loss arises from catabolism of amino acids after absorption from the digestive tract. A review of the literature indicates that ruminal outflow of protein N is essentially equivalent to N intake, i.e., 100% efficient (Ipharraguerre and Clark 2005). However, individual values ranged from a low of 65% to those exceeding 100%. Efficiencies greater than 100% result from net recycling of urea N from blood. Compared with ruminal efficiencies, post-absorptive efficiencies of conversion of absorbed amino acids to milk protein are generally less than 50% (Hanigan et al. 1998; Rius et al. 2010). Either a reduction in RDP or in metabolizable protein while holding productive use constant is required to improve efficiency.

Urinary N losses by dairy cows decrease linearly with decreasing dietary CP levels. These reductions can sometimes be achieved with minimal or no effects on yield or composition of milk and milk protein. Olmos Colmenero and Broderick (2006) and Cyriac et al. (2008) recorded MNE exceeding 35% in cows fed diets with CP contents of only 13.5% or 13.6%, respectively. Milk yield by cows fed diets containing 15.0 to 18.5% CP was unaffected by CP level, while their N excretion and urinary N proportions increased simultaneously as dietary CP increased (Groff and Wu 2005).

Given that recycled urea N from blood can be recaptured in microbial protein, reducing N intake in the form of RDP is an attractive method of reducing urinary N excretion (Kebreab et al. 2002). Feeding excess RDP results in greater ruminal N and milk urea N concentrations and increases urinary N losses (Hristov et al. 2004). Utilizing a combination of prediction equations (urine volume) and actual analyses (urine composition), de Boer et al. (2002) demonstrated the importance of the ruminal N balance (OEB in the Dutch feeding system) in reducing N losses in dairy cows. Increasing OEB from 0 to 1,000 g per cow per day

linearly increased urinary N excretions. With high-producing cows, lowering dietary CP may in certain situations result in decreased milk yield (Broderick 2003), which would be unacceptable to most producers and nutritionists in the field, but this is not the case for all studies (Cyriac et al. 2008; Li et al. 2009). Performance effects, when recorded, often appear to stem from the complex interactions of protein with DM and energy intake (Huhtanen and Hristov 2009). In the absence of any changes in energy intake, microbial and total N flows from the rumen tend to decline as dietary RDP is reduced (Cyriac et al. 2009). Such a loss in N flow can compromise animal performance. Lee and Hristov (2010b) observed a significant decrease in milk yield (by 3 kg d^{-1}; $P<0.04$) when a 14% CP diet was fed, compared with one containing 16% CP. These effects could be avoided by providing sufficient metabolizable protein (by increasing dietary RUP), or by supplementing cows with synthetic, ruminally protected amino acids that were limiting milk production (Broderick et al. 2008). The former approach would generally not result in any improvements in overall N efficiency, but the latter could be expected to improve N efficiency, if production losses are prevented. Broderick (2005), for example, demonstrated that supplementing the diet with ruminally protected methionine maintained milk yield and MNE increased from 26 to 34% as dietary CP decreased from 18.6 to 14.8%. Methionine supplementation of low CP diets can also decrease the proportion of urinary N in total excreted N (Krober et al. 2000).

Carbohydrate source and availability in the diet can also have a significant effect on ruminal N utilization and, provided the ruminally captured N is used to synthesize milk protein, a reduction in urinary urea output. Increasing the dietary net energy of lactation concentration from 1.55 to 1.62 Mcal kg^{-1} decreased urinary urea N excretion and increased MNE (from 25 to 30%), whereas increasing the dietary CP level from 15.1 to 18.4% had the opposite effect, i.e., it increased urinary urea N excretion and decreased MNE (Broderick 2003). Rius et al. (2010) observed similar responses when feeding diets varying in overall energy content but with constant metabolizable protein levels. Increasing dietary concentrate to 72% (DM basis) resulted in more efficient utilization of ruminal NH$_3$ for milk protein synthesis, but this did not correspond to reduced urinary N losses and did not reduce NH$_3$ emissions from manure compared with feeding a diet containing 52% concentrate (Agle et al. 2010a).

There are several challenges with current protocols for calculating dairy cattle protein and amino acid requirements. The first is related to the assumption that the conversion of metabolizable protein to milk protein and other metabolic functions are fixed values. For example, it is assumed that the conversion efficiency for milk protein is 65% (NRC 2001), yet considerable evidence in the literature indicates that the efficiency is ≤45%

[calculated from Eq. 4.3 of Doepel et al. (2004)] and that it is a variable function of supply rather than a fixed value (Whitelaw et al. 1986; Hanigan et al. 1998). Assuming such high and static conversion efficiency prevents selection of protein feeding levels that would maximize the return on dietary protein inputs. Clearly, marginal returns to incremental additions of dietary protein near the plateau are much lower than the returns from early incremental additions to the diet.

A second deficiency in our current requirement system is the assumption that a single nutrient limits production (NRC 2001). Emerging research suggests that at the cellular level, protein synthesis rates are regulated in an integrative manner based on signals arising from cell sensing of amino acid supply, energy supply, and hormonal signals (Jeyapalan et al. 2007; Suryawan et al. 2007; Appuhamy et al. 2009; Bell et al. 2009). These results are consistent with the observations of independent effects of metabolizable protein and dietary energy in the study of Rius et al. (2010) and suggest that much greater efficiencies can be achieved given the correct mixture of individual amino acids, energy supply, and hormonal state. Baker (1996) demonstrated that the efficiency of post-absorptive use of N in pigs can reach 85% when the supply of AA are well matched to tissue needs. A similar level of efficiency may be possible in ruminants given adequate knowledge of the system which would dramatically reduce urinary N output and NH$_3$ volatilization from manure.

Dietary CP levels and effects on urinary urea excretion are directly related to NH$_3$ emissions from cattle manure. Paul et al. (1998) reported a linear decrease in manure NH$_3$ losses with decreasing dietary CP concentration. Similarly, reducing the CP content of the diet (Frank et al. 2002) or its RDP concentration (Van Duinkerken et al. 2005) effectively reduces volatile N losses from manure. The effects of metabolizable protein supply are similar. Weiss et al. (2009) reported that increasing dietary metabolizable protein increased NH$_3$-N produced per gram of manure mainly because of increased urinary N excretion with a significantly smaller contribution of fecal N. Smits et al. (1995) fed dairy cows two diets differing in OEB (40 vs. 1,060 g d^{-1}) and reported a significant increase in urinary urea-N concentrations and NH$_3$ emissions from manure (by 39%) with the high-OEB diet. Külling et al. (2001) demonstrated that at 17.5% CP in the diet, N losses from manure after 7 wk of storage were from 21% (slurry) to 108% (urine-rich slurry, i.e., a urine:feces ratio of 9:1) greater than N losses from manure when cows were fed 12.5% CP, with respective NH$_3$ emissions rates of 163 and 42 µg m^{-2} s^{-1}. Feeding diets low in protein (13.5 to 14% CP) to dairy cows resulted in significantly lower NH$_3$ release from manure compared with the high CP (15 to 19%) diets (Frank and Swensson 2002; Frank et al. 2002). Agle et al. (2010b) also showed a remarkable effect of dietary CP on the

NH_3-emitting potential of dairy manure. In that study, decreasing dietary CP concentration from 15.4 to 13.4 or 12.9% decreased cumulative (15-d) NH_3 emissions from manure by up to 38%. Similarly, Lee and Hristov (2010b) reported a 45% reduction in the NH_3-emitting potential of manure with low (14%) vs. high (16%) CP diets. The effect of these diets on NH_3 emissions from manure-amended soil was also investigated by applying manure to lysimeters collected from a Hagerstown silt loam (Lee et al. 2010). Ammonia volatilization was significantly greater from high- than from low-CP manure-amended soil [areas under the cumulative NH_3 emission curves were 114.8 and 56.8 (mg $NH_3\,m^{-2}$ per min) × h, respectively; Fig. 8]. These experiments clearly demonstrated that manure from dairy cows fed reduced CP diets had decreased NH_3 emitting potential a response that was carried through to the manure when it was land applied.

AMMONIA EMISSIONS FROM BEEF CATTLE FEEDLOTS

Only a small percentage of the N consumed by feedlot cattle is retained in animal tissue and as a result, 80 to 90% is excreted in urine and feces. Nitrogen can be lost via volatilization as NH_3, nitrous oxide, dinitrogen gas, amines, or other N-containing compounds. As in dairies, the quantity and form of N loss from a feedlot are affected appreciably by nutrition, manure-handling processes, type of confinement system, and environmental conditions (McGinn et al. 2003; Todd et al. 2006, 2008, 2009). The vast majority of beef cattle in North America are fed in open, unpaved lots; however, semi-confined, total-confinement, and pastoral systems are still used in North America and throughout the world.

Sources of Emissions

With typical beef cattle finishing diets, approximately 10 to 20% of N intake is retained in animal tissues, 30 to 50% of fed N is excreted in the feces, and 40 to 70% of fed N is excreted in urine (Cole and Todd 2009; Fig. 6b). As noted earlier, it appears that the primary source of NH_3 emission from the pen surface of feedlots is urine spots. This hydrolysis and emission is very rapid, being pH, moisture, and temperature dependent, but may be complete within 96 h of urine deposition.

Atmospheric Ammonia Concentrations at Feedlots

Atmospheric NH_3 can occur in a variety of forms: as a gas, (NH_3), a fine particulate (i.e., $(NH_4)_2SO_4$ and NH_4NO_3), or as a liquid (i.e., NH_4OH in clouds and fog). The partitioning of these phases is highly variable and dependent upon other compounds in the atmosphere. However, within a few kilometers of feedlots, most NH_3/NH_4^+ will be in the gaseous stage and/or particulate associated (Langford et al. 1992). Ammonia also has a tendency to form strong hydrogen bonds with water and thus absorb/adsorb on the surfaces of most materials exposed to air. This can lead to high background and ghosting effects due to retention and intermittent release of NH_3 from surfaces such as sample tubing or other sampling equipment.
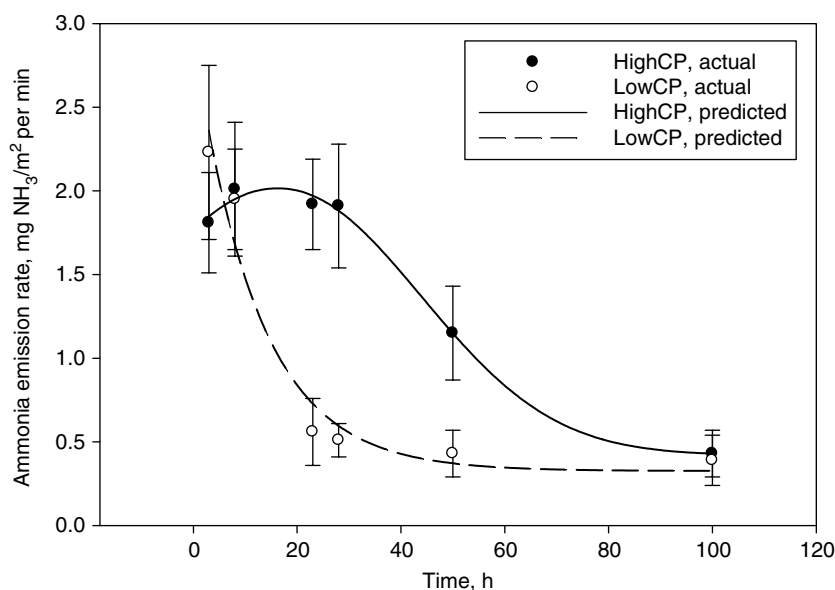
Fig. 8. Ammonia volatilization from soil amended with manure from dairy cows fed diets with high (HighCP, 16%) or low (LowCP, 14%) crude protein content (from Lee et al. 2010). Symbols are measured values (± SE). Lines are predicted values (peak, modified Gaussian and exponential decay regression models, respectively).

Background NH_3 concentrations at feedlots typically range from <1 to 40 $\mu g\,m^{-3}$ (Todd et al. 2005). Although atmospheric NH_3 concentrations at feedlots vary greatly depending upon sampling site, sampling time, sampling height, temperature, wind speed, and turbulence, average daily concentrations measured at a variety of feedlots tend to agree (Table 2) and range from approximately 100 to 2000 $\mu g\,m^{-3}$. Measured maximum concentrations rarely exceed 2000 $\mu g\,m^{-3}$. Ammonia concentrations decrease rapidly downwind of feedlots (Miner 1975) approaching background concentrations in less than 800 m (McGinn et al. 2003; Cole and Todd, unpublished data). Deposition of NH_3 downwind of feedlots has ranged from 15 to 365 $kg\,ha^{-1}$ annually, decreasing with distance from the yard, (Hutchinson and Viets 1969; McGinn et al. 2003).

Ammonia Emissions from the Feedlot Pen Surface

Only a few studies have reported NH_3 emissions from typical North American feedlots using N balance and/or micrometeorology techniques (Table 3). This is in part due to the difficulties in measuring these factors in an open lot situation. Several studies estimated NH_3 emission factors for livestock based on typical European production systems (Asman 1992; Battye et al. 1994). In general, these cattle were either grazing highly fertilized pastures or were in semi-confinement barns, conditions very different from typical North American cattle feeding operations.

Ammonia flux rates from feedlots, measured using various micrometeorology procedures, have ranged from 3.6 to 88 $\mu g\,m^{-2}\,s^{-1}$ and estimated NH_3 emission factors (per animal) have ranged from 50 to 283 $g\,d^{-1}$. These rates are comparable with, but generally greater than, emission factors for dairy operations (Table 1). Nitrogen volatilization losses measured using micrometeorology and/or N balance methods have ranged from 28 to 72% of fed N, which is higher than the estimates for dairy cows. The higher values for finishing beef cattle than dairy cattle are probably due to a combination of factors including the following: (1) a greater proportion of fed N is retained in product in dairy than beef cattle; (2) a greater proportion of fed N is lost in urine in beef cattle; (3) less organic matter is excreted in feces of finishing beef cattle; and (4) air turbulence and movement is greater in open lot feedlots than dairy barns. Emissions in winter were approximately 50% of those in summer. However, Rhoades et al. (2008) reported that NH_3 fluxes at a Texas feedlot were highest in April, which may reflect a loss of NH_4^+ that accumulated in the manure pack over winter as spring temperatures increased (Cole et al. 2009a, b; Cole and Todd 2009).

Based on measurements made only in the afternoon, Hutchinson et al. (1982) estimated annual NH_3 emissions in Colorado feedlots at 33.6 kg per head capacity using a flux-gradient method. Using a general box model, James et al. (1997) estimated annual NH_3 emissions of 59 ± 65 kg per head capacity during the summer in California. Todd et al. (2008) based annualized emission factors on either animals fed (head yr^{-1}) or animal weight gain produced (Mg yr^{-1}); annual NH_3 emission factors were 20.2 kg per head fed or 73.4 kg per Mg weight gain, respectively.

Ammonia flux from feedlots has a diel pattern with the lowest flux typically occurring just before dawn and the highest flux in the early afternoon (Hutchinson et al. 1982; McGinn et al. 2003, 2007; Todd et al. 2005, 2008; Flesch et al. 2007). McGinn et al. (2003) noted average NH_3 flux rates that ranged from a low of 36 $\mu g\,m^{-2}\,s^{-1}$ at approximately 0400 to a high of 129 $\mu g\,m^{-2}\,s^{-1}$ at 1400, with a second smaller peak at 2200. These diel patterns can be partially explained by the high correlation between NH_3 flux and sensible heat flux as noted by McGinn et al. (2007), expressed as [$y = 0.434x + 55.344$, $r^2 = 0.84$; where $y =$ ammonia flux as $\mu g\,m^{-2}\,s^{-1}$ and $x =$ heat flux as $W\,m^{-2}$].

The NRC (2003) suggested that a single "emission factor" for NH_3 is difficult to justify because so many environmental factors can affect emissions and that process-based models are more appropriate. However, the USEPA (2005) currently proposes an NH_3 emission factor of 13 kg $head^{-1}$ annually for feedlot cattle or 23% of N entering the feedlot. Based on data from dairies and swine lagoons, the USEPA proposes that 20% of N entering manure stockpiles, 43% of N entering storage ponds, and 17 to 20% of manure N applied to farm land is lost as NH_3.

Ammonia Losses from Retention Ponds and Lagoons

Facilities designed to collect runoff from feedlots can also be a source of NH_3 emissions. Runoff from most open-lot feedlots is collected in retention ponds and allowed to evaporate. In some cases solids may be removed in settling basins before the runoff enters the retention pond. Gilbertson et al. (1970) reported that 3 to 6% of excreted N was lost in runoff from the feedlot surface. Bierman et al. (1999) noted similar values for diets containing 8 and 20% roughage, although N runoff exceeded 20% of N excreted when all-concentrate diets were fed. Vanderholm (1975) reported that 20 to 70% of N was lost from aerated and anaerobic manure storage facilities before it was spread on fields. Using open path NH_3 lasers and an inverse dispersion model, Flesch et al. (2007) reported that NH_3 flux rates from a Texas feedlot retention pond ranged from 2 to 41 kg NH_3 per hour. Pond NH_3 emissions averaged 8.5 kg ha^{-1} daily and represented only 5% of emissions from the pens. Todd et al. (2008) estimated that annual emissions from the retention pond were 0.9 kg per head fed or 3.2 kg per Mg of body weight gain. The low NH_3 flux from feedlot retention ponds, in comparison to dairy or swine lagoons, is probably due to a combination of factors including low total N and NH_3-N

concentrations and relatively low pH. Cole and Todd (unpublished data) noted total Kjeldahl N concentrations in feedlot retention ponds of 980 mg L^{-1} in the summer and 310 mg L^{-1} in the winter. Total NH_4^+-N concentrations averaged 17 and 83 mg L^{-1} when effluent pH averaging 8.6 and 7.2, respectively. Bussink and Oenema (1998) and Harper et al. (2000) indicated that some N may be lost from lagoons/retention ponds via reduction of nitrate to nitrous oxide (N_2O) and dinitrogen gas. A number of possible chemical and biological mechanisms may exist for formation of dinitrogen gas in anaerobic lagoons (Jones et al. 2000), but their significance in feedlot retention ponds is unclear.

Losses During Composting

Composting has become a popular method to decrease the volume and weight of livestock manure and to produce a product that is often more acceptable to farmers as a fertilizer. During a 100- to 120-d composting period, the weight and volume of manure can be decreased by 15 to 70% (Inbar et al. 1993; Lopez-Real and Baptista 1996; Eghball et al. 1997). Eghball et al. (1997) reported that 19 to 45% of the N present in manure was lost during composting, the majority of which presumably as NH_3. Using changes in the N:P ratio of manure that was placed in compost windrows and the N:P ratio of "finished" compost, Cole and Todd (unpublished data) estimated that 10 to 20% of N was lost during composting. The USEPA currently assumes that 1 to 10% of N entering compost systems is lost as nitrous oxide (IPCC 2006; USEPA 2009b).

Losses on Pasture

Using ^{15}N-labeled urea, Thompson and Fillery (1998) noted that approximately 30 to 50% of urinary N applied to pasture residues in October, November, January, March, and April was lost as NH_3 within 2 wk of application. When applied to growing pasture in August and September, NH_3 losses accounted for 10 to 30% of total applied N. Lockyer (1984) reported that following the application of urine to grass swards, NH_3 emission rates exceeded 100 mg m^{-2} h^{-1} during the first 2 h, but decreased to less than 25 mg m^{-2} h^{-1} within 24 h. It might be expected that NH_3 losses from urine excreted onto the surface of confined feedlots would equal or exceed these rates, given that a greater quantity of fecal microbial urease would be present. Hutchings et al. (1996) reported that in a grazing system, only 11 to 16% of N input was lost as NH_3. Annual losses were 4 kg per head for beef cattle. Fourteen to 25% of the NH_3 loss occurred from grazed areas and 28 to 47% occurred from the manure storage system.

Factors Affecting Ammonia Emissions from Feedlots

As noted previously, NH_3 emission from feedlots is a complex biochemical and physical process controlled by factors such as air temperature, media temperature,

moisture, media pH, wind speed, atmospheric NH_3 concentrations, media NH_3/NH_4^+ concentration, microbial activity, and urinary N excretion (Varel 1997; Petersen et al. 1998; Cole et al. 2009a, b). From 50 to 80% of excreted N is in urine and this quantity typically increases as CP concentration in the diet increases (Erickson et al. 2000; Cole et al. 2005; Todd et al. 2006).

The extensive nature of feedlots makes NH_3 fluxes even more affected by environmental conditions than dairies. Hutchinson et al. (1982) indicated that NH_3 emissions from a Colorado feedlot ranged from 0.64 kg ha^{-1} h^{-1}, measured 3 d after a 15-cm snowfall, to 2.37 kg ha^{-1} h^{-1} under hot, dry conditions. Rainfall events appear to depress NH_3 emissions temporarily, followed by an increase in emissions as the pen surface dries (Hutchinson et al. 1982; Todd et al. 2005, 2008). Baek et al. (2006) reported that NH_3 flux was correlated exponentially to air temperature at 6 m, by the equation [flux, μg m^{-2} $s^{-1} = -1.46 + 7.96e^{0.077temp}$; $r^2 = 0.57$; temp is temperature at a height of 6 m in °C]. This would explain why numerous studies have reported that N volatilization losses in the summer are approximately two-fold higher than losses in the winter (Erickson et al. 2000; Todd et al. 2005, 2008). A 2-yr analysis of mean monthly per capita emission rates at two commercial feedlots demonstrated that emissions fit closely to the Arrhenius model, with Q10 temperature coefficients ranging from 1.31 to 1.56 (Todd and Cole, unpublished data). Lower N volatilization in winter also accounts for the greater concentration of N in feedlot manure and the greater recovery of fed N in manure during this season (52.1%) as compared with summer (35.2%) (Cole and Todd 2009). Using a laboratory system, Dewes (1996) reported that over a 14-d period, NH_3 emissions from a straw/manure slurry mixture had two peaks corresponding to the population dynamics of proteolytic and amino acid-degrading bacteria. Ammonia emissions were both abiotically and biotically induced. Changes in pH had the greatest effect on abiotically induced NH_3 emissions. At pH of 6 and 7.5 abiotically induced emissions were low whereas at pH 9, as much as 10% of the initial N was lost as NH_3. Decreasing pH from 7.5 to 6 decreased biotically induced emissions, whereas increasing the quantity of straw (i.e., carbon source) decreased both the biotic and abiotic emissions. Increasing the temperature increased biotic emissions. After 4 d of storage at temperatures of 30 and 40°C, the amount of microbially digestible carbon available was adequate to permit almost total reincorporation of NH_4^+ into microbial protein.

Abating Ammonia Losses

Three basic approaches have been used to decrease NH_3 losses from cattle operations: (1) diet/ration manipulation, (2) manure/slurry treatment, and (3) capture and treatment of emitted gases. Each approach has a multitude of possible and available technologies. Using a computer model of whole-farm dairy operations, Kohn

et al. (1997) estimated that improvements in animal diets and management that increase the conversion of feed N to animal product by 50% would increase total farm N efficiency by 48% and decrease N losses per unit of product by 36 to 40%. It has been estimated that decreasing N losses involved in manure collection, storage and application would improve whole-farm N efficiency by 13% and decrease N losses by 14% (Monteny and Erisman 1998).

Effect of Diet on Ammonia Emissions from Feedlots

Bierman et al. (1999) fed diets with neutral detergent fibre contents of 10% (all concentrate), 13% (7.5% roughage), or 28% (wet corn gluten feed, 41.5% of diet DM). Under those conditions, 45 to 57% of the N fed was volatilized, and the proportion decreased with increasing dietary roughage content. This was most likely due to a partial shift in N excretion from urine to feces. Similarly, Adams et al. (2004) reported that additions of organic matter to the pen surface and more frequent pen cleaning could reduce N volatilization losses and conserve N in manure. However, both methods appreciably increase manure management costs. Kellems et al. (1979) noted that grain source (corn vs. sorghum vs. barley) and concentration (25, 50 or 75% of diet DM) affected NH_3 emissions primarily via their effects on fecal pH.

The quantity and source of dietary N can affect nutrient excretion markedly, because of differences in the site and rate of protein digestion. Using an in vitro system, Cole et al. (2005) did not find a significant effect of dietary CP source (urea or cottonseed meal) on NH_3 emissions. However, in vitro NH_3 losses from a mixture of steer feces and urine (1% of daily excretion) increased exponentially as dietary CP concentration increased. Using the integrated horizontal flux method, Todd et al. (2006) noted similar effects when feces and urine were applied to a simulated feedlot surface. Similarly, James et al. (1999) reported a 28% decrease in apparent NH_3 volatilization in Holstein heifers fed diets containing 9.6% CP rather than 11% CP.

Feeding distillers' grains (DGS) has had variable effects on N volatilization losses from feedlot pens (Cole et al. 2008; Todd et al. 2009). Feeding DGS at high concentrations in the diet can increase NH_3 emissions due to an increase in dietary N intake and subsequent increase in urinary N excretion. However, at relatively low intakes ($<15\%$ of diet DM), feeding DGS generally results in modest increases in dietary N intake. Feeding lower concentrations of DGS shifts some N excretion from the urine to the feces, decreases fecal and manure pH, and provides additional organic matter on the pen surface (Cole et al. 2008).

As animals mature, there is a shift in the proportion of carcass protein and fat retained that results in a decrease in dietary protein requirements (as a percent of diet DM). Thus, it may be possible to decrease protein concentrations late in the feeding period (i.e., phase feeding) without adversely affecting animal performance. Cole et al. (2005) reported that in vitro NH_3 emissions from feces and urine increased with days on feed, due primarily to increased urinary N excretion. Erickson et al. (2000) fed feedlot steers diets with a CP content held constant at 13.4% or altered in phases from 13.4 to 10.5% CP, and observed no effect on animal performance. However, N excretion was decreased by phase feeding both in calves and in yearlings. Estimated N volatilization was lower for phase-fed steers than for controls, measured at 62 vs. 73 g head^{-1} d^{-1} for calves, and 108 vs. 158 g head^{-1} d^{-1} for yearlings. Estimated N volatilization losses were decreased approximately 25% in cattle phase-fed steam-flaked corn-based diets (Cole et al. 2006).

Using regression analysis and N balance data obtained from commercial feedlots over a 1-yr period, Cole and Todd (2009) noted that when metabolizable protein intake was less than animal requirements, the N volatilization losses averaged approximately 40 g head^{-1} d^{-1}. This value was similar to the calculated endogenous urinary N excretion rate and suggests this may be the minimum NH_3 emission rate that can be obtained via dietary manipulations. When decreasing dietary CP to decrease NH_3 emission, potential negative effects on animal performance and costs of gain must also be considered.

Manure/Slurry Treatments

Ammonia volatilization from the feedlot surface and waste retention facilities can potentially be decreased through the use of additives such as bedding, acids, alum, calcium chloride, adsorbents (zeolite, humate) or urease inhibitors (Shi et al. 1999; Varel et al. 1999; Parker et al. 2005). Unfortunately, each of these methods has distinct disadvantages (increased manure mass, increased manure P, increased sulfate emissions, increased Cl content, short effect period, etc.) that may limit their use in commercial beef production. Combinations of compounds that inhibit NH_3 losses via different mechanisms (urease inhibition and adsorption, for example) may be more effective than single compounds (Cole et al. 2007a).

Improving pen drainage may be one strategy that lowers NH_3 emissions while simultaneously benefiting animal performance. Other approaches such as more frequent manure collection and/or the application of inhibitors/attractants may potentially decrease NH_3 emissions, but are not economically feasible under present production conditions.

Capture and Treatment of Emitted Gases

Research on the capture and/or treatment of gases emitted from CAFO has routinely involved the use of solids/liquid separation, permeable or semi-permeable covers on lagoons, and/or the use of biofilters to trap emissions as they exit via the ventilation system of the

animal house (Powers 1999; VanderZaag et al. 2008). The use of these methods is limited to facilities that use total confinement and/or liquid manure handling systems; typically swine and dairy operations. Their use in beef cattle feedlots, which are typically open lot and use solid, rather than liquid, manure management systems have not been studied.

MODELING AMMONIA EMISSIONS FROM DAIRY AND BEEF PRODUCTION SYSTEMS

Measurement of farm-level NH_3 emissions is difficult and expensive. In a recent project sponsored by the dairy industry, gaseous emissions, including NH_3, from several dairy facilities were monitored continuously over a 2-yr period at a cost of approximately $1 million per farm (NAEMS 2006). This national study focused on housing facilities, with a few measurements made from manure storage. Other on-farm emission sources such as field-applied manure were not measured. Facilities and management practices vary widely among farms; therefore data collected from specific farms cannot be directly applied to other farms or generally applied across all farms. Due to the difficulty and expense in measuring gaseous emissions from farms, a process-based modeling approach has been recommended for quantifying farm emissions of NH_3 and other important gaseous compounds (NRC 2003).

Process-based modeling is a modeling procedure in which system processes are mathematically represented at an appropriate level of detail to capture the important dynamics and interactions among components. Other common modeling approaches use emission factors or simple empirical relationships to quantify various emission sources within a production system. Process-based modeling provides a more robust approach, because this type of mechanistic model is more responsive in predicting the effects of management changes.

Research over the past century has enabled a good understanding of the mechanisms by which volatile compounds in solution form, migrate, react, and ultimately volatilize to the atmosphere. As this understanding evolved, mathematical models were developed and validated to represent these processes accurately. Through adaptation of these relationships, emissions such as NH_3 from manure can be predicted for livestock farming systems. Predicted emissions from each important source are summed to determine a total farm emission. By evaluating theoretically developed models with the limited data available from on-farm measurements, a robust model can be produced for evaluating a wide range of farm production practices.

Modeling of Emission Processes

Ammonia emission from a material such as manure involves five important processes: urea hydrolysis, dissociation, diffusion or mass transfer through the solution, aqueous-gas partitioning, and mass transport away from the manure surface to the atmosphere. Each of these processes is well understood and mathematical relationships are available to quantitatively represent their effects in manure.

About half or more of the N excreted by cattle is in the form of urea, which is rapidly hydrolyzed to form NH_3 N. The rate of urea hydrolysis is dependent upon temperature, pH, and the concentration of urea in the manure solution. Muck (1982) found that Michaelis-Menten kinetics described the variation in urease activity in feces as a function of urea concentration. The maximum urease activity and the Michaelis-Menten constant increased with temperature between 10 and 40°C, and the activity decreased linearly on both sides of a pH range of 6.8 to 7.6. Since the pH of cattle manure normally falls within this range, pH has little influence on urease activity in cattle manure (Sommer et al. 2006). Urease activity has been modeled as proportional to urea concentration with an exponential increase with temperature (Sommer et al. 2006).

The distribution of TAN between NH_3 and NH_4^+ in a solution such as manure, i.e., TAN dissociation, can be modeled using equilibrium principles (Stumm and Morgan 1996). Hashimoto and Ludington (1971) developed a relationship to predict the NH_3 fraction in poultry manure, which has been widely applied to predict the dissociation of TAN in all manure types. More recently, Montes et al. (2009) used a theoretical approach to develop a model that more accurately represented NH_3 dissociation in buffered NH_4^+ solution and dairy cattle manure. The NH_3 fraction in a manure solution is a function of pH and a dissociation constant that increases exponentially with temperature.

Henry's Law relates the NH_3 in a solution to that in air contacting the solution surface. The Henry's Law constant, defined as the ratio of gaseous NH_3 concentration in air in equilibrium with that in solution, is exponentially related to temperature. A number of equations have been used to represent this relationship with a wide range in predicted values (Ni 1999; Montes et al. 2009). Montes et al. (2009) developed a model based upon theoretical principles and found that this model, along with their dissociation constant model, predicted NH_3 concentration in air in equilibrium with the TAN content in cattle manure better than previous models.

In a large volume of manure, such as in a storage tank, aqueous phase migration within the tank becomes important. Diffusion and dispersion processes must be modeled to predict the migration of TAN from the high concentration at lower depths toward the lower concentration at the surface. The rate of this migration can be predicted using a mass transfer, diffusion, or dispersion coefficient, depending on the degree of mixing and the level of detail of the model (Incropera 2006). Relationships are well developed for modeling the diffusion rate of solutes through a solution; however, this process is complicated by simultaneous transport

and reactions of multiple chemical species (Blanes-Vidal et al. 2009).

The movement of NH_3 away from the manure surface into the surrounding atmosphere can be modeled using the principles of mass transfer. The rate of transfer, quantified as a mass transfer coefficient, is a function of the wind speed over the surface, temperature of the manure and air, and the geometry of the surface in relation to air movement (Perry et al. 1997; Incropera 2006; Montes et al. 2009). A number of empirical relationships have been used to predict NH_3 transfer from manure (Ni 1999). Most of these were based upon an NH_3 transfer model developed by Haslem et al. (1924) for conditions much different from that of a flat manure-covered surface. Principles are again well established for deriving a model for the mass transfer coefficient based upon the properties of the emitted compound and air as the transfer media. Montes et al. (2009) developed a relationship that was found to work well in predicting NH_3 emission from cattle manure when used along with their derived relationships for the dissociation and Henry's Law constants.

Modeling of Farm Processes
By linking models for the emission processes, emission rates can be predicted for each of the major NH_3 sources on farms. The four major sources are housing facilities, manure storage, field applied manure, and direct deposits on pasture. The same principles and relationships can be used to predict emissions from each, but there are differences in the way these relationships are applied.

Housing facilities include free stall barns, tie stall barns, feedlots, and bedded pack barns. For predicting emissions from these facilities, manure is typically represented as a thin layer with a uniform concentration of TAN where diffusion is neglected. Urea hydrolysis is an important part of this emission source, where the excreted urea is converted to TAN. Emission can then be predicted through an integrated model of the dissociation, aqueous-gas equilibrium, and mass transfer processes. A major difference among housing facilities is bedding and the area soiled by the manure. As manure is spread over more area, the emission per animal increases. The soiled area in a tie stall barn is typically about half that in a free stall or bedded pack barn, and the area per animal in a feedlot is about double that in free stalls. For feedlot and bedded pack facilities where manure accumulates, diffusion through the manure pack may also be important. When a gradient in TAN concentration forms within the manure layer, the emission rate at the surface is influenced by the diffusivity of the TAN species in the manure. Another important consideration for manure in housing facilities is the pH on the manure surface. As described above, with animal movement and continuous application of fresh feces and urine, surface pH is dynamic and variable across the surface confounding the prediction of NH_3 emissions.

When long-term storage of manure is used on livestock farms, the storage facility is another important source of NH_3 emission. Manure is stored in liquid, slurry, and solid forms depending upon the manure management system used. By the time manure is placed into storage, most of the urea has been converted to TAN, so any remaining urea hydrolysis results in negligible NH_3 emissions. Bedding and manure solids can be separated to form liquid manure (<5% DM). This liquid portion, containing most of the TAN, is typically stored in an earthen basin or tank. With wave motion, the liquid remains relatively well mixed and diffusion has a minimal role. When manure is stored as slurry (7–12% DM), less mixing occurs within the storage and diffusion through the manure plays a greater role. If the slurry is pumped into a storage tank or basin, a crust may form on the manure surface. This crust provides additional resistance, further reducing the rate of TAN migration to the surface. Manure mixed with bedding material may also be stored as semi-solid or solid manure (>12% DM) in stockpiles. In this form, diffusion through the manure becomes a major constraint to the emission rate. For each type of storage, the same set of relationships describing dissociation, diffusion, aqueous to gas partitioning, and mass transport away from the manure surface can be used to predict emission rate. Differences among storage systems arise due to design, differences in agitation and emptying, variation in the diffusion properties of the manure and the constraint they place on the movement of TAN to the surface.

Manure can be applied to crop land through various methods including surface and subsurface application. When applied to a soil surface, the manure is in a thin layer where remaining TAN readily volatilizes as NH_3. If no incorporation is used, most of the TAN remaining on the surface is normally volatilized within a day (Rotz 2004). When liquid manure is applied or if rain occurs soon after application, a portion of the manure N infiltrates into the soil reducing volatile loss. As described above, temperature also has a major role. With colder temperatures (<10°C), the emission processes slow considerably. Application techniques, such as incorporation through cultivation, are sometimes used to enhance the infiltration of surface-applied manure (Rotz et al. 2010a). By increasing infiltration, there is less TAN remaining on the surface to volatilize to NH_3. The emission of surface-applied manure N can be predicted using relationships for dissociation, diffusion, aqueous to gas partitioning, and mass transport from the manure surface. Manure can also be applied by subsurface injection. The TAN applied in the soil binds to soil particles minimizing NH_3 emission. With direct injection, NH_3 emissions are relatively low emissions arising mainly from minor amounts of manure that remain exposed at the soil surface (Rotz et al. 2010a).

When grazing is used, NH_3 emissions occur from fecal and urine deposits in the pasture. Since most of the TAN comes from urea, urine deposits account for about 90% of total NH_3 emissions (Rotz 2004). A portion of the urine (about 30–50%) infiltrates into the soil where the urea hydrolyzes and the TAN binds to the soil. The remaining portion settles on plant and soil surfaces where it comes in contact with urease, and is hydrolyzed to TAN that volatilizes. Ammonia formation and emission can again be modeled to include dissociation, aqueous to gas partitioning, and mass transport into the surrounding air. These processes generally result in volatilization of the surface NH_3 within 24 h. If rain occurs during this time, the TAN concentration is diluted and infiltration is increased, both of which reduce NH_3 emissions (Rotz and Oenema 2006).

Whole-farm Evaluation

Due to important interactions among the various NH_3 sources on the farm, NH_3 emission must be evaluated at the whole-farm level. For example, if mitigation strategies are used to reduce emissions in the barn, then more TAN is in the manure leaving the barn, potentially increasing storage and field application losses. Therefore, reducing emissions from housing or storage facilities has little benefit if the field application process is not also properly managed to reduce emissions. The reduction of NH_3 emissions also interacts with other parts of the farm. For example, reducing NH_3 emissions will increase nitrate leaching and denitrification losses of N if the additional N from reduced emissions is not appropriately managed for plant uptake. Reducing N losses may also increase crop yield and protein content, both of which will affect feed quality, animal production, and manure nutrient excretion.

Several models have been developed and used to evaluate the N cycle in livestock farms and interactions with other parts of the farm. Many of these models use an empirical modeling approach where emission factors or simple relationships are used to predict NH_3 emissions. Examples include DyNoFlo (Cabrera et al. 2005), Farm N (Hutchings et al. 2005), DairyWise (Schils et al. 2006), and Agrammon (Menzi et al. 2008). Since the relationships or factors used are developed from empirical data for specific conditions, they are limited in their scope of application and their responsiveness to management changes. For example, they may not properly represent emission levels across different climates, manure characteristics, and management practices. These types of models can provide useful tools for evaluating the specific conditions under which they were developed, but they are not versatile for evaluation over a broader range of practices and conditions.

A more robust approach is to use the mechanistic models described above to simulate NH_3 emissions within farm systems. With this process-level modeling approach, emission predictions are more sensitive to changes in climate and management. Therefore as the farm conditions are modified, the model responds and accurately adjusts emission levels.

Hutchings et al. (1996) developed a dynamic model to predict NH_3 emissions from grazing livestock farms. Process-level relationships were integrated to predict emissions from animal houses, stored manure slurry, field applied slurry, and urine deposits on pasture. This NH_3 emission model was incorporated into a dynamic farm simulation model called FASSET that was used to evaluate N taxation scenarios for European farms (Berntsen et al. 2003). Pinder et al. (2004a) adapted Hutchings' model to create a tool used to estimate dairy cattle emissions throughout the United States. Rotz and Oenema (2006) also expanded Hutchings's model to improve the prediction of management effects on NH_3 emissions along with other environmental impacts and farm economics in the Integrated Farm System Model. In another effort, Zhang et al. (2005b) developed a process-based NH_3 emission model for confined animal feeding operations including dairy, beef, swine, and poultry.

Although these process-level models provided effective tools for evaluating climate and management effects on NH_3 emissions, they did not fully represent the effects of urease activity, the interaction among multiple chemical species, and the effects of organic matter of the manure on dissociation and transport processes. Recent work by Montes et al. (2009) has developed improved relationships describing these processes for use in the NH_3 emission component of the Integrated Farm System Model.

The Integrated Farm Systems Model provides the most comprehensive tool for evaluating NH_3 emissions along with other environmental impacts and the economics of dairy, beef, and crop farms. Crop production, feed use, and the return of manure nutrients back to the land are simulated for up to 25 yr of weather for a selected location (Rotz et al. 2009a). Growth and development of crops are predicted on a daily time step based upon soil water and N availability and weather. Tillage, planting, harvest, storage, and feeding operations are simulated to predict resource use, timeliness of operations, crop losses, and nutritive changes in feeds. Feed allocation and animal responses are related to the nutritive value of available feeds and the nutrient requirements of the animal groups making up the herd. Simulated performance is used to determine production costs, incomes, and economic return.

Along with NH_3 emission, other losses to the environment are predicted. Denitrification and leaching losses from soil are related to the rate of movement through the soil profile as influenced by soil properties, rainfall, and the amount and timing of manure and fertilizer applications (Rotz et al. 2009a). Erosion and phosphorus losses are functions of terrain, soil conditions, and tillage and manure application practices (Sedorovich et al. 2007). Carbon dioxide, methane, and nitrous oxide emissions are tracked from crop,

animal, and manure sinks and sources to predict the net greenhouse gas emission (Rotz et al. 2010b). Following the prediction of nutrient losses, whole-farm balances of N, P, K, and C are determined as the sum of all nutrient imports in feed, fertilizer, deposition, and legume fixation minus the exports in milk, excess feed, animals, manure, and losses leaving the farm.

The Integrated Farm System Model has been used to evaluate and compare NH_3 emissions, other environmental impacts, and economics of a wide range of production systems. Recent studies have included comparisons of conventional and organic dairy production (Rotz et al. 2007), confinement feeding and grazing based dairy production (Rotz et al. 2009b), and an evaluation of surface and subsurface manure application methods (Rotz et al. 2010a). This model has also been used to determine the feasibility of combining several N conserving technologies on dairy farms including fecal and urine separation on barn floors, an enclosed manure storage, subsurface injection of field-applied manure, and controlled grazing (Rotz et al. 2006).

Process-level simulation provides a powerful tool for evaluating NH_3 emissions and their interaction with other farm processes and ultimately the profitability of livestock production systems. Work continues on the refinement of emission models and their integration in whole-farm models. As mitigation strategies are developed, their feasibility must be evaluated in light of all environmental and economic impacts. This is best done with the use of process-based farm simulation.

CONCLUSIONS

Societal pressure and the goal of achieving sustainable animal production necessitate reduction of NH_3 emissions from dairy and beef cattle operations. Even with the complexity of factors regulating NH_3 emissions, there is sufficient evidence that emissions from dairy and beef cattle facilities are significant. Direct and indirect methods for measuring NH_3 emissions are available and fairly accurate for the specific farm, but emissions factors can be extremely variable depending on manure management and environmental conditions. Data summarized in this review indicate average whole-farm NH_3 emission factors of 59 and 119 g animal^{-1} d^{-1} for dairy and feedlot operations, respectively. Manure composition (affected primarily by the diet fed) and manure collection and storage are the main factors affecting NH_3 emissions from an animal operation. Reducing crude protein concentration in cattle diets is perhaps the most feasible method for mitigating these losses. Availability of relatively inexpensive, high-protein feeds (by-products of the emerging biofuel industry), however, can lead to a significant overfeeding of protein to feedlot and dairy cattle, thus contributing to even greater N concentration in manure and farm NH_3 emissions. Addressing these challenges and developing effective mitigating techniques along with further elucidating the specific role of NH_3 in fine particulate matter formation,

downwind N deposition, and impact on ground water nitrate require funding and collaborative research efforts.

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