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Ammonia emission from dairy cow buildings: a review of measurement techniques, influencing factors and possibilities for reduction

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Abstract

Because ammonia from livestock production may contribute substantially to environmental pollution, emission from all possible sources (housing systems, manure storage, manure application, outside grazing) should be reduced. Ammonia emission from dairy cow buildings is estimated to be 28% of the total emission from Dutch agriculture. The purpose of this study is to make an analytical inventory of ammonia emission data of dairy housing systems and to assess possibilities for its reduction, based upon the analysis of processes and factors involved in the production and volatilisation of ammonia.

Mass balance methods for the determination of air exchange rates for naturally ventilated dairy cow buildings that are based upon natural or introduced tracers may have good potential for application in emission studies.

In today's dairy husbandry, differences occur in housing system, floor type and manure collection and manure storage system. Ammonia emission levels for cubicle (loose) houses are higher (20–45 g day^{-1} per cow) than for tie stalls (5–27 g day^{-1} per cow), although variation in emissions per housing type is large. Integration of knowledge of ammonia emission related processes and factors will support a more detailed analysis of differences and variation, and will allow an optimisation of possibilities for emission reduction. Substantial emission reductions of up to 50% for cubicle houses with slatted floors can be achieved through each of the following measures: flushing of floors with water or diluted formaldehyde, optimised feeding strategies, and slurry acidification. Highest reductions are possible through V-shaped, solid floors (52%) as a single measure, or in combination with flushing with water (65%) or diluted formaldehyde (80%). Providing that drawbacks are solved, nation wide introduction of one or more these measures will lead to a maximal reduction of the NH_3 emission in The Netherlands with 18 kton per year. To achieve the emission reduction goals set by the Dutch government, additional emission reduction for all agricultural sources must be realised.

Keywords: animal nutrition, dairy cattle, environmental pollution, floor construction, legislation, manure treatment, measurement techniques, modelling

Introduction

During the past decades, livestock production has been intensified both in numbers of livestock and in production level, following an increased input of minerals through feed stuffs and chemical fertilisers. As a consequence, emission of ammonia (NH_3) to the atmosphere from livestock production related sources (housing systems, manure storage, land spreading of manure, outside grazing) has increased drastically. The emission of NH_3 from agricultural activities in Europe, excluding the former USSR, has doubled between 1950 and 1986 (Asman *et al.*, 1988), whereas for The Netherlands this increase was by a factor 2.5 (ApSimson *et al.*, 1987). This increased NH_3 emission has substantially contributed to the exceeding of critical loads for nitrogen (N) deposition in many European countries, leading to eutrophication and soil acidification related environmental stress (Heij & Schneider, 1991; Heij & Erisman, 1997).

In The Netherlands, for example, about 46% of the potential acid deposition is caused by emission of NH_3 (Erisman & Bleeker, 1997), mainly originating from agriculture (Anonymous, 1996). To avoid NH_3 related environmental damage, its emission must be reduced with 70% in 2005 relative to the emission level in 1980 (204 kton; Anonymous, 1996), being the reference year for Dutch NH_3 legislation.

In 1995, 60% of the Dutch agricultural NH_3 emission originated from cattle husbandry. Ammonia emission from cattle housing systems, including storage, was estimated at 45 kton (37 kton for dairy; 8 kton for other cattle) in 1995, being approximately 34% (28% for dairy) of the national emission (Anonymous, 1996). In addition to the law enforced advanced slurry application techniques and covering of outside slurry storages, legislation is prepared for animal buildings with low emissions to achieve the reduction goals.

Improved and structured knowledge of NH_3 related processes and factors can be used as a tool to improve insight in differences in levels of NH_3 emission and to support legislation concerning and research into optimisation of emission abatement strategies for cattle buildings. The availability of accurate methods for measurement of NH_3 emissions from agricultural sources is important in the framework national and international emission studies (Asman, 1995; Anonymous, 1994a) and for strategic monitoring and research purposes (e.g. assessment of emission reduction measures). Naturally ventilated animal buildings, being the most common type of dairy cow housing, require in this framework special attention, because of the technical complexity of measurement of its ventilation rates.

The objective of this paper is a literature-based discussion on the origin of NH_3 release in dairy cow buildings and possibilities for measurement and abatement of NH_3 emissions. In this perspective the following issues are addressed:
- theory of NH_3 development in dairy cow buildings
- state of the art in measurement technology for animal buildings
- inventory of current housing systems for dairy cows and their NH_3 emissions
- possibilities for reduction of NH_3 emission based upon the way they interfere with emission related processes and factors
- synthesis and conclusions.

Processes and parameters influencing NH_3 release in dairy cow buildings

N excretion in faeces and urine

Nitrogen plays a basic role in the life cycle, physiological processes, production and body maintenance of animals. All N that is taken up with the feed and not retained in the animal body is excreted in faeces and urine. Tamminga (1992) estimated that, of the daily N intake by an average Dutch dairy cow, 29% is excreted in faeces, 50% in urine and 19% in milk, while 2% was deposited in body reserves. Non-protein N compounds, mainly being in the form of urea, are excreted with urine. Ammonia in dairy cow buildings is for the largest part produced following urea hydrolysis (Muck & Steenhuis, 1981). The amount of urea N relative to the total N content of dairy cow urine depends on physiological factors like diet composition and production level and is between 59–89% for cattle fed with grass or grass and maize silage, including protein supplement (Bristow *et al.*, 1992). An increasing surplus of degradable protein in the diet will result in a higher rate of N excretion with urine (Van Vuuren *et al.*, 1993), whereas the volume of urine produced is related to the intake of N, potassium (K) and sodium (Na) (Van Vuuren & Smits, 1997). This volume will affect the urination frequency. Whitehead (1995) made an inventory of urine production (volume, urination frequency) by dairy cows and of typical values for faecal and urinary N excretion. In this inventory, covering many international literature sources, it is discussed that all parameters mentioned above show a large variation, mainly related to differences in diet (including water consumption), production level, breed and management. Urine production, urination frequency, urea N concentration in urine and N excretion with urine, expressed per cow, range from 10–40 l day^{-1}, 8–12 day^{-1}, 2–20 g l^{-1} and 80–320 g day^{-1}, respectively. Faeces mainly contain organic N compounds (e.g. undigested protein; daily N excretion 50–200 g per cow). Ammonia production from these compounds in dairy cow buildings is relatively unimportant (Muck & Steenhuis, 1982), because of low mineralisation rates. Mineralisation may play a role when the slurry is stored, either inside or outside the house, for longer periods of time and especially at higher temperatures (Patni & Jui, 1991).

Urea hydrolysis

Urea hydrolysis, catalysed by the enzyme urease, follows the Michaels Menten kinetics for basic enzymatic conversion processes (see e.g. Muck & Steenhuis, 1981). Urease is produced by micro organisms that are abundantly present in faeces and thus also upon surfaces that are frequently fouled with faeces, like floors (Ketelaars & Rap, 1994). The following equation represents urea hydrolysis in a liquid environment (e.g. urine on the floor, urine in the straw bed or slurry in the pit):

$$CO(NH_2)_2 + H_2O \xrightarrow{urease} 2NH_3 + CO_2 \qquad [1]$$

The rate of urea hydrolysis and thus the ammonium production rate depends on the urea concentration in the urine and the maximal rate of enzymatic urea hydrolysis at high urea concentrations, also called 'urease activity'. Urease activity is temperature related. Muck & Steenhuis (1981) reported complete urea conversion within 1 day after urine deposition upon fouled floors at temperatures above freezing point. Furthermore, Elzing & Monteny (1997a) showed that all urea in urine applied on a fouled slatted floor element was converted within approximately two hours at temperatures of 10 °C or higher. This means that urea hydrolysis is completed fast under conditions found in practice. Moreover, urease activity levels in commercial dairy cow buildings are very high (Braam & Van Den Hoorn, 1996), making the substrate (urea) availability the limiting factor. Measures that reduce emissions from fouled floors may therefore focus on lowering the initial urea concentration in the urine via nutrition or very frequent dilution (e.g. by flushing floors with water) or on a drastic reduction of the urease activity.

Dissociation

In the liquid, ionised (ammonium; NH_4^+) and unionised (ammonia; NH_3) equilibrilize (equation 2):

$$NH_3 + H_2O \xleftrightarrow{pH,\,T} NH_4^+ + OH^- \qquad [2]$$

The amount of NH_3 relative to total ammoniacal N (TAN: sum of NH_3 and NH_4^+) in the liquid is determined by the, positively with temperature ('T') related, acid dissociation constant (K_a) for NH_3 and by the pH (Loehr, 1973). For NH_3 dissociation in aqueous solutions at 20 °C, K_a is $3.982{*}10^{-10}$ (Weast *et al.*, 1986), whereas for more concentrated solutions, like slurries, an adapted – much lower – K_a-value was found ($0.81{*}10^{-10}$; Hashimoto, 1972). The influence of pH is very pronounced. At pH values below 6–7, nearly all TAN in the liquid is present in ionised, non-volatile form (NH_4^+). Above pH 7, the fraction of NH_3 increases greatly and at pH values of 11 or higher TAN is mainly in the form of NH_3. Data reported by Elzing & Monteny (1997a) showed that the urine on a fouled floor has a pH of around 8.6, whereas that value was also assumed for the pH of the top layer of slurry in the pit, being the places where volatilisation takes place. At these pH levels, up to 50% of TAN is present in the form of volatile NH_3 (Groot Koerkamp & Elzing, 1996), mainly depending on temperature. Acidification of slurry and urine to a level of below pH 6 is a very effective way to lower the NH_3 release.

Volatilisation

Volatilisation of NH_3 is convective mass transfer from the boundary of urine or slurry and air to the air above the floor or above the slurry in the pit. The amount of volatile NH_3 depends on equilibrium between NH_3 in the liquid ('l') and in the gas phase ('g') at that boundary (equation 3), following Henry's Law:

$$NH_3\,(l) \xleftrightarrow{T} NH_3\,(g) \qquad [3]$$

This equilibrium is strictly temperature dependent; higher temperatures result in a higher amount of gaseous NH_3.

Ammonia volatilisation rate (equation 4) is the product of the NH_3 mass transfer coefficient and the difference in concentration or partial pressure of gaseous NH_3 ('g') between boundary ('bound') and air above the boundary ('air').

$$NH_3\,(g,bound) \xrightarrow{T,v} NH_3\,(g,air) \qquad [4]$$

The mass transfer coefficient for NH_3 depends on temperature ('T') and air velocity ('v') at the boundary. Haslam *et al.* (1924) developed a general relationship for NH_3 in a film reactor. It was found to be applicable for dairy cow housing systems too (Muck & Steenhuis, 1981). More empirically determined mass transfer coefficients for NH_3 in the framework of animal husbandry emissions research were reported in recent studies (Svensson & Ferm 1993; Arogo *et al.*, 1996), but their application was not studied for other conditions and situations than that they were developed for.

Elzing & Monteny (1997a) showed that, at values for urease activities found in dairy cow buildings, NH_3 volatilisation is the highest at approximately two hours after urine deposition upon floors. Furthermore, NH_3 volatilisation from a urine puddle was found to continue for 15 hours or more, depending on environmental conditions. Interfering in the volatilisation process itself to reduce NH_3 release in dairy cow buildings will have to focus on reducing temperature, through cooling of floor and slurry surfaces, and air velocity, by minimisation of airflow inside the building.

Measurement techniques for NH_3 emission from livestock buildings

The emission of NH_3 from a building is defined as the product of air exchange rate and the difference in NH_3 concentrations in incoming and exhaust air. Methods and equipment for measurement of air exchange rates and gas concentrations are discussed below.

Air exchange rates

Direct methods. For mechanically ventilated animal buildings, the anemometer or measurement ventilator installed in the ventilation shaft (Van Ouwerkerk, 1993) is commonly used to determine air exchange rates directly. Wind tunnel calibration is necessary to relate the anemometer response (rotations per time unit) with the actual air exchange rate.

Continuous monitoring of pressure differences over all ventilation openings of the building is useful as a direct method for naturally ventilated animal buildings. The basis of this method is Bernoulli's Law, relating the ventilation rate over an opening to the surface area of the opening and the square root of the pressure difference over the opening (Van Ouwerkerk, 1993). It is still in an experimental stage.

Indirect methods. Indirect methods, using heat balances or tracer gas mass balances, have become ready for use during the past years. The basic principle of the heat balance method (Van 't Ooster *et al*. ,1994; Van Ouwerkerk, 1993) is that the change in temperature of the air volume inside the building is the net result of heat production (e.g. by animals or external heating) and heat losses, mainly through convective heat transfer through the structure, and ventilation. To calculate ventilation rate, all other heat production and loss terms have to be known. Ventilation rate for a certain time step directly follows from measured change in air temperature inside the building per time unit, given the effective heat capacity of the air inside the building.

The principle of mass balance methods for tracer gasses is basically the same as for the heat balance approach. The ventilation rate follows from the net result of tracer gas production and losses, assuming no gas transport through the construction elements of the house. Depending on the goal of the measurements, methods for natural and synthetic tracer gases are:
– a variable, known production rate, e.g. when production rate from the source of the tracer gas cannot be controlled (natural tracer gas)
– a constant production rate (continuous dosage of a synthetic tracer gas)
– rate of decay (certain amount of synthetic tracer gas introduced in the house at t=0)

In the framework of emission surveys, continuous determination of the ventilation rate is required. This makes the first two methods the most appropriate. In Van Ouwerkerk (1993), a detailed description is given of the variable production rate method using the CO_2 mass balance. This method requires a CO_2 production model for animals (Van Ouwerkerk & Pedersen, 1994). Introduced tracer gases like carbon monoxide (CO; Demmers *et al.*, 1998), sulphur hexa fluoride (SF_6) and nitrous oxide (N_2O) can be used in the method of constant production rate.

Measurement equipment for gas concentrations

Tracer gases. Van 't Klooster *et al.* (1996) give an overview of technical possibilities for the measurement of tracer gas concentrations in the framework of NH_3 emission studies. For the purpose of accurate measurement of emission levels or process studies, N_2O, CO and CO_2 concentration can be measured best with monitors based upon the Non Dispersive Infra Red principle (NDIR). Basic elements of such monitors are an infrared emitter and receiver. Different gasses show absorption of specific wavelengths in the IR spectrum. The measured absorption or extinction in the IR-spectrum is a direct measure for the concentration of the gas under survey. They can be used for specific gases (Demmers *et al.*, 1998), when using the appropriate filters, or for multi gas measurements (Van Ouwerkerk, 1993). Cross sensitivity with e.g. water vapour may affect measurement accuracy. When SF_6 is used, concentrations need to be measured with a gas chromatograph (GC).

Ammonia. Besides NDIR monitors, a nitrogen oxide (NO) monitor in combination with a high temperature catalyst stainless steel converter is commonly used in The Netherlands for continuous measurement of NH_3 concentrations in livestock buildings. This method is described in detail by Van Ouwerkerk (1993) and Groot Koerkamp *et al.* (1998). In the catalyst converter, NH_3 is converted to NO. The main reason for this is that NO is reasonably inert, while NH_3 in the air sampling tubes may be lost e.g. by dissolving in water drops or absorption at the tube surface. NO monitors use the principle of a chemo-luminescence reaction between NO and ozone. Wyers *et al*. (1993) describe the development and application of a continuous flow denuder for NH_3 concentration studies, basically for ambient NH_3 concentration levels but also for a wider application (e.g. in livestock buildings; Van Ouwerkerk, 1993). It has a much lower detection limit than the measurement techniques described previously. The basic process in a denuder is chemical absorption/desorption using counter flows of sampled air and acid absorption solutions. After a desorption procedure, the NH_3 concentration is measured on-line conductometrically.

When continuous measurement of NH_3 concentration is not required, a system of continuous air sampling and accumulation in an acid solution (e.g. nitric acid) in combination with titrimetric determination of the amount of NH_3 captured afterwards in a laboratory or accumulation in passive samplers can be used (Van Ouwerkerk, 1993).

Evaluation

The advantage of the heat balance is the fact that only the air temperature inside the building has to be measured, which is fairly simple compared to measurement of tracer gasses concentrations. Drawbacks are related to the need for models to predict heat production terms (animals) and losses through the surrounding structure.

Assuming no gas transport through the structure, advantages of the use of tracer gasses lie in the limited number of loss terms, since this can only be through ventilation (assuming no accumulation in manure, the animal or parts of the internal structure). On the other hand, the density of the tracer gas should be close to air density to allow the assumption of perfect mixing. When using the CO_2 mass balance, no tracer gas has to be introduced in the building, meaning that the measurement system can be restricted to gas sampling and analysis only. When synthetic tracer gasses are used, a dosage system has to be installed and operated. Moreover, synthetic tracer gasses may have other drawbacks like toxity (CO), specific masses differing from air (N_2O, CO) and the possibility of gas production from unknown or unexpected sources (N_2O; nitrification/denitrification of nitrogen compounds).

Scholtens *et al.* (1996) validated the use of CO_2 and CO mass balance methods against the method of anemometers placed in the exhaust shafts in a mechanically ventilated dairy cow building. The CO_2 method underestimated the ventilation rate by 18%, whereas the CO method showed no significant difference with the anemometer method. The model for CO_2 production by the animals (Van Ouwerkerk & Pedersen, 1994) was found to be the most important source of the underestimation by using the CO_2 mass balance (Scholtens *et al.*, 1996). Van Ouwerkerk & Pedersen (1994) proposed to increase the respiration quotient to improve the CO_2 production model for dairy cows. Demmers *et al.* (1998) showed that applicability of the CO mass balance is quite good, except under conditions of high ventilation rates in naturally ventilated buildings. Under these conditions, mainly caused by high outside wind speeds, the difference in CO concentrations between air entering and leaving the building appeared to be too small to be measured accurately and thus to allow accurate estimation of the ventilation rate.

For continuous and exact measurement of NH_3 emissions from mechanically ventilated buildings, an anemometer in combination with the converter + NO monitor or with a NDIR monitor is to be preferred, whereas the combination of synthetic tracer gas and specific monitors or a GC is the best procedure for naturally ventilated buildings.

Besides methodology and measurement technique, measurement strategy (design of hardware and protocol for measurements) is of great importance when carrying out emission studies for naturally ventilated cow buildings. Incomplete mixing of volumes of air inside the house leads to spatial variability in gas concentrations. This aspect has to be studied before the measurements start in order to design the sampling system (number and location of sampling points) for air inside the house correctly. When designing the protocol for measurements, detailed knowledge of the emission process benefits minimisation of the number of measurements and its duration. Mechanistic modelling of the processes relevant for NH_3 emission (Muck & Steenhuis, 1981; Monteny *et al.*, 1998) and the application of statistics (De Boer, 1993) may contribute to this.

Dairy cow buildings: floor and manure handling systems and NH_3 emission

Two main types of housing systems for dairy cows can be distinguished: loose housing and tie stalls. In loose housing, the two major sub-systems are cubicle housing systems and non-cubicle or (deep) litter and straw systems. Functional elements of loose housing systems are a non-restricted (open, straw bed) or partly restricted (cubicles) lying area, a walking area and a feeding area. For tie stalls systems, these functional elements are combined (Anonymous, 1994b). Floor type, manure handling and indoor manure storage facilities are the major characteristics that are relevant from NH_3 emission point of view. Table 1 presents an overview of dairy cow housing systems, subdivided by these characteristics. Except for straw based systems where farmyard manure (FYM) is produced, manure is present in the form of slurry. Ammonia emission data are given to the extent that reliable data were available from different literature sources. Conditions under which the measurements were carried out (ventilation system and measurement principle of ventilation rate) are reported. Data are discussed in the following paragraphs.

Loose housing systems

Cubicle houses with slatted floors are the most common for dairy cows in The Netherlands (Anonymous, 1995) and some other European countries (Anonymous, 1994a). Inside, under floor pits are present for slurry storage. Kroodsma *et al.*

Table 1. Housing systems for dairy cows, floor, manure handling and manure storage characteristics, NH_3 emission (g day^{-1} per cow) and measurement conditions.

Housing	Floor	Manure	Manure	NH_3	Ventilation		Reference
System	Type	Handling	Storage	Emission	System*1)	Method *2)	
Loose housing							
* cubicle	Slats	No	Deep pit	32–45	M	Anemom	Kroodsma *et al.*, 1993
				20–42 *3)	N	CO_2	Groot Koerkamp *et al.*, 1997
				40	N	CO_2	Van 't Ooster, 1994
				26	N	Estimate	Pfeiffer *et al.*, 1994
	Flat, solid	Scraping	Outside	25	N	Estimate	Pfeiffer *et al.*, 1994
				32	N	CO	Demmers *et al.*, 1998
	Sloped, solid	Scraping	Deep pit	25 *4)	M	Anemom	Huis In 't Veld *et al.*, 1994
* non-cubicle	Flat, solid	Tractor	Outside	30	M	Anemom	Groenestein & Reitsma, 1993
Tie stalls	Slats	No	Deep pit	9–14	M	Anemom	Groenestein & Montsma, 1991
		No	Shallow pit	5–12	N	Estimate	Mannebeck & Oldenburg, 1990
	Gutter	Scraping	Outside	27	N	Estimate	Pfeiffer *et al.*, 1994
				6–21 *3)	B	CO_2	Groot Koerkamp *et al.*, 1997

*1): M = mechanical ventilation; N = natural ventilation; B = both ventilation principles
*2): anemom = anemometer; CO_2, CO = gas mass balance method; estimate = estimated air exchange rates
*3): emission data corrected for mean outside temperature
*4): emission standardised for 15 °C

(1993) found NH_3 emission from a mechanically ventilated cubicle house varying from 32 to 45 g day^{-1} per cow at an inside air temperature range of 12 to 18 °C. Groot Koerkamp *et al.* (1997) measured NH_3 emissions from 16 cubicle dairy cow buildings during a large survey in 4 European countries (UK, The Netherlands, Denmark and Germany). Ammonia emission was measured during 24 h under winter and summer conditions. After correction for mean outside temperature, average NH_3 emission per country ranged from 20 (Denmark) to 42 (The Netherlands) g day^{-1} per cow. The observed variation between 4 similar dairy cow buildings per country and between countries can be regarded as a combination of systematic and natural variation, mainly caused by differences in climate, diets, details in the building designs and management. Other emission data for naturally ventilated cubicle buildings with slurry storage beneath the slatted floor were found to amount 40 g day^{-1} per cow (Van 't Ooster, 1994) and 26 g day^{-1} per cow (Pfeiffer *et al.*, 1994). Emission data were not corrected for temperature.

Inclined shallow pits beneath the slats are common for cubicle houses in the US (Collins & Wilson, 1994). In these systems, slurry is continuously removed from the house by gravity and stored outside, e.g. in a slurry lagoon. Emission data in literature were lacking for such housing systems.

Cubicle housing systems with flat or sloped solid floors are found in various countries. A solid floor type implies that faeces and urine have to be removed regularly (e.g. with scrapers) and collected in an under floor pit or in an outside storage. When a flat solid floor is present, there may be a longitudinal incline towards a dorsally situated collection gutter to allow slurry removal by flushing and additional outside storage (e.g. in a lagoon; Fulhage & Martin, 1994). Ammonia emission levels for cubicle houses with flat solid floors with scrapers and outside slurry storage of 24.5 and 31.6 g day^{-1} per cow were reported by Pfeiffer *et al.* (1994) and Demmers *et al*. (1998), respectively. Data were not corrected for temperatures. Sloped, solid floors may be designed V-shaped, with a lateral slope, so urine is drained through a small gutter, longitudinally situated in the middle of the floor (Swierstra *et al*., 1995). The slope may also be to one of the sides of the walking alley (Moore & Hegg, 1980). Ammonia emission for a V-shaped solid floor with a 3% lateral slope was 24.5 g day^{-1} per cow, corrected for a reference temperature of 15 °C (Huis in 't Veld *et al.*, 1994).

Non-cubicle loose housing systems, operated with a straw bed or a concrete floor, are less common than loose housing systems with cubicles. When a straw bed is used, faeces and urine collected often remain in the house for a longer period of time. Removal of the collected faeces and urine – indicated as farm yard manure (FYM) – can be by hand or by a scraper attached to a tractor. Ammonia emission for a mechanically ventilated house containing 40 dairy cows and 18 head of young stock, at an average temperature of 9 °C, was on average 30 g day^{-1} per animal (not corrected for temperature; Groenestein & Reitsma, 1993).

Tie stalls

In tie stalls, faeces and urine are collected either as slurry in an under floor pit covered with concrete or steel slats, or in a shallow gutter where faeces and urine are separately collected. In the US, tie stalls are often equipped with inclined shallow pits beneath the slats (Graves *et al*., 1984). Removal of the faeces, optionally collected in a layer of straw in the gutter (FYM), is carried out by hand or by a scraper, whereas urine is drained off by gravity. FYM is usually stored outside. Daily NH_3 emission for a commercially operated, mechanically ventilated tie stall for dairy cows, with slurry storage in a pit with a depth of 1 m behind the animals, varied with temperature (15 to 19 °C) from 9 to 14 g per cow (Groenestein & Montsma, 1991). Ammonia emission from 16 naturally and mechanically ventilated tie stalls, observed in 4 European countries in the framework of the international survey described previously, varied from 6 to 21 g day^{-1} per cow (corrected for mean outside temperature) (Groot Koerkamp *et al.*, 1997). Based upon an estimated ventilation rate, Mannebeck & Oldenburg (1990) and Pfeiffer *et al.* (1994) reported emissions of 5 to 27 g NH_3 day^{-1} per cow (not corrected for temperature) for a large number of naturally ventilated tie stalls, measured under various outside temperatures. As described for emissions from cubicle housing systems, ranges in NH_3 emission from tie stalls observed appear to be large due to systematic and natural variation in emission determining factors.

Measures to reduce NH_3 emission from dairy cow buildings

Measures that reduce the NH_3 emission from a dairy cow house are based on engineering, nutrition or management. They influence one or more of the parameters that play a role in the emission related processes. Main themes are: (1) reduction of the urea concentration of urine by nutritional measures; (2) dilution of urine on floors and removal from floors; (3) slowing down the urea hydrolysis on floors; (4) control of pH; (5) reduction of mass transfer of NH_3 from urine and slurry; and (6) reduction of air exchange between pit and house.

Reduction of the urea concentration of urine by nutritional measures

Altering the diet is regarded as an effective and direct way of achieving a reduction of the urea concentration in the urine. Smits *et al*. (1995) compared the effect on the NH_3 emission of two diets in a commercial cubicle house with 34 lactating, highly yielding dairy cows in a repetitive experiment over 126 days. The diets differed in nitrogen content, resulting in a daily intake per cow of rumen degradable protein (RDP) with the "low-N" diet of 40 g, and of 1060 g with the "high-N" diet. Salt was added to the low-N diet to obtain similar urine production volumes. As a result, the concentration of urea nitrogen for the low-N diet was 42% lower than for the high-N diet, whereas the emission of NH_3 was reduced with approximately 39%. The results are in good accordance with the findings by Elzing & Monteny (1997b). They reported a linear relation between the urea concentration and the NH_3 emissions in trials, conducted in a scale model of a dairy cow house, where a fouled slatted floor element was sprinkled with urine from groups of lactating cows fed with different diets. In another experiment (Smits *et al.*, 1997) similar to the one mentioned previously (Smits *et al.*, 1995), salt was added to the high-N diet to increase both N excretion in urine and urine production, at a comparable urinary urea concentration. The emission reduction by the low-N diet was approximately 20%, mainly caused by the reduced number of urinations per cow.

Dilution and removal of urine on floors

Indirect lowering of the urea and TAN concentration is achieved through flushing floors. Adding water results in a dilution of the urine on the floor and of the slurry in the pit. Besides dilution, removal of urine from the floor surface is a feature of flushing systems. The frequency of the flushing actions and the amount of water used per flushing determine the potential NH_3 emission reduction. Frequent flushing results in more frequent removal of urine, whereas flushing with more water results in an increased dilution.

By flushing slatted floors, NH_3 emission was reduced by a maximum of 17% (De Boer *et al.* ,1994; Ogink & Kroodsma, 1996). Even though different amounts of water (up to 110 l day^{-1} per cow) and flushing intervals (once every 1–3.5 h) were used, no relationship was found between emission reduction and those variables. Relative to unflushed slatted floors, spraying a V-shaped solid floor with 6 l of water day^{-1} per cow at a scraping and flushing frequency of once every two hours resulted in a 65% reduction of the NH_3 emission (Braam *et al.*, 1997b). The effects of amounts of water used and flushing and scraping frequencies on the emission reduction for a V-shaped solid floor were reported by Huis In ’t Veld *et al*. (1994) and De Boer *et al.* (1994). They reported that flushing with 50 l of water day^{-1} per cow every 2 hours directly after the scraping action resulted in an emission reduction of 34% compared to only scraping of the solid floor. Increasing the scraping and flushing frequency to once every hour did not result in a significant higher emission reduction. Emission was reduced to 14% at a reduced water use to 28 l day^{-1} per cow combined with an increased scraping and flushing frequency of once every hour. From this data we may conclude that, contradictory to findings for slatted floors, emission reduction and water use are positively correlated for V-shaped solid floors.

At flushing frequencies mentioned above, flushing will not have had a major effect on the urea hydrolysis process through dilution of urea, because urea is usually hydrolysed within 2 h after urine deposition on floors. To be effective from that point of view, continuous flushing would have to be operated or the flushing frequency would have to be related to the urination frequency. Both options were for technical reasons not investigated.

Slowing down urea hydrolysis

Slowing down the urea hydrolysis process can be achieved through temperature reduction or inhibition of the enzyme urease. For dairy cow buildings, data on cooling of floor and slurry surfaces and effects on NH_3 emission were lacking in literature. Urease inhibitors are well known in rice production (Keerthisinghe & Freney, 1994) and are sometimes used to lower NH_3 emissions from feedlots (Varel, 1996). Their applicability in cow buildings has not been investigated. Emission reduction data were obtained from experiments on flushing floors with diluted formaldehyde. Scraping and flushing were combined and conducted hourly and every two hours, respectively. Ammonia emission reduction for slatted floors and V-shaped solid floors, relative to the emission from a cubicle house with slats, was 50% (Ogink & Kroodsma, 1996) and 87% (Bleijenberg *et al.*, 1995), respectively, using daily volumes of 19 l and 34 l of a diluted formaldehyde solution per cow. These data indicate that urea hydrolysis had been reduced to very low values. Furthermore, Ketelaars & Rap (1994) successfully removed floor-bound urease activity in dairy-cow houses by rinsing the floor with a hydrochloric acid solution, consequently reducing NH_3 emission to very low values.

Control of pH

Lowering the pH at the emitting surfaces (floor, slurry in the pit) by addition of acid has shown to be quite effective in reducing NH_3 emissions from slurry. A reduction of 37% was reported by Bleijenberg *et al.* (1995) in experiments where pH of the slurry, stored in a pit under the slatted floor, was reduced to 4–4.5 by regular addition of nitric acid. Even higher reductions of up to 60% were achieved by a combination of acidification of slurry in a shallow pit and regular flushing of the slats with the acidified slurry (Kroodsma & Ogink, 1997).

Reduction of mass transfer

Possibilities for influencing convective mass transfer of NH_3 are through reduction of temperature and air velocity at the emitting surfaces (floor and slurry) and of the area of the emitting surface (Elzing & Monteny, 1997b). Findings with temperature reduction are previously described. Influencing air velocity in naturally ventilated cow buildings is hard to achieve, because a system for regulation of the ventilation rate is not present or not operated. Except through solid floors, possibly leading to a reduction of air velocity in the pit (see next sub-paragraph), reduction of air velocities by climatisation is therefore not regarded to be a practical option for emission abatement.

Reduction of the area of floors and pit is only possible when the housing system is changed. Ammonia emission was reduced by approximately 10% when the fouled floor area per cow was reduced from 3.5 to 2.5 m^2 in an adapted design for a dairy cow house with cubicles (Metz *et al.*, 1995). For a tie stall with a fouled floor area of approximately 1 m^2 per cow and a reduced pit area, emission reduction was 28% compared to a cubicle house (Metz *et al.*, 1995).

Reduction of air exchange between pit and house

The area for air exchange between the pit and the air inside the house depends on the floor type used (Braam *et al.*, 1997a) and by parameters causing air exchange (e.g.

ventilation system, stack effect due to temperature gradients between slurry and inside air; see e.g. Bruce, 1975). For slatted floors, this area is approximately 20–25% of the total floor area (Anonymous, 1989). In cow buildings equipped with solid floors, the only possibility for air exchange is through the openings at each end of the alleys through which scraped slurry is deposited in the pit. Intermediate openings might be required at increased floor length. The reduced air exchange is an important factor in the emission reduction found for these type of floors relative to slatted floors. As a consequence of reduced air exchange, transport of NH_3 volatilised to the air inside the pit to the air inside the house is hindered (Braam *et al.*,1997b). Furthermore, it might also cause lower air velocities at slurry level, leading to a lower volatilisation (Elzing & Monteny, 1997b). Also the enhanced accumulation of NH_3 in the air inside the pit may contribute to a reduced volatilisation. Swierstra *et al.* (1995) reported emission reductions between 48% and 52% for solid, V-shaped floors. Similar reductions were found by Braam & Van den Hoorn (1996), for the same floor but with high slurry level and a wooden construction to prevent airflow in the pit. Comparability of those data is hard, because of differences in experimental conditions (season, year).

Table 2 presents a schematic overview of the interaction between NH_3 emission reducing measures and processes and parameters. In this overview, emission reduction potential is expressed relative to dairy cow buildings with cubicles, slatted floors and under floor slurry storage.

Prospects of different emission reducing measures

Nutrition

Practical possibility for reduction of the nitrogen excretion in urine is replacement of a part of the grass silage in the cow's diet by feed stuffs with a low nitrogen content, e.g. maize (Valk *et al.*, 1990; Dewhurst & Thomas, 1992). However, dairy cow diet manipulation to reduce NH_3 emission should focus on lowering the urinary nitrogen concentration in the urine by lowering the N surpluses in the diet rather than by increasing the volume of urine produced or the frequency of urination (e.g. through the addition of salt; Smits *et al.*, 1997). In that perspective, the intake of water, induced by the amounts of N and salts in the diet is of importance.

Other possibilities for the reduction of the nitrogen content of the diet are through improved grassland management and grazing. Bussink (1994) showed that reduction of the N fertilisation rate of grassland resulted in a significantly lower NH_3 emission during grazing of dairy cows. This was mainly caused by a reduced excretion of N. Expectedly, feeding of grass silage from the grassland with the reduced fertilisation rate will also reduce NH_3 emission in the dairy cow house. However, no data are available to support this. Bussink & Oenema (1998) calculated that part time grazing during the summer (cows kept inside during night) leads to an increase in NH_3 emission on a farm scale by 10% compared to full time grazing. Because the cows then

Table 2. Overview of the working principle of emission reducing measures and reduction of the NH_3 emission reported in literature (in % compared to slatted floors).

Measure	Process involved	Control factor	Maximal Reduction	Reference
Feedings strategies	urine and faeces production	urea concentration	39	Smits *et al.*, 1997
Slurry handling:				
* flushing with water	enzymatic conversion	urea concentration	17	Ogink & Kroodsma, 1996
* formaldehyde flushing	enzymatic conversion	urease activity	50	Ogink & Kroodsma, 1996
* slurry acidification	dissociation	pH	37	Bleijenberg *et al.*, 1995
+ additionally flushing slats with acidified slurry	dissociation	pH	60	Kroodsma & Ogink, 1996
Floor systems:				
* V-shaped solid floors	aur exchange/volatilisation	air velocity	52	Swierstra *et al.*, 1995
+ flushing with water	enzymatic conversion	urea concentration	65	Braam *et al.*, 1997b
+ formaldehyde flushing	enzymatic conversion	urease activity	80	Bleijenberg *et al.*, 1995
* reduced slatted floor area	volatilisation	emitting area of floor/pit	10	Metz *et al.*, 1995
Housing systems:				
* tie stalls	volatilisation	emitting area of floor/pit	28	Metz *et al.*, 1995

stay inside the house for a longer period of time, more slurry (faeces and urine) is produced inside the house, causing extra emission from the house. Moreover, because more slurry needs to be applied to the field, emission from land spreading increases.

Flushing systems

A major drawback of flushing is the amount of water added to the slurry. At an average daily slurry production of 50 l per cow, flushing of slatted floors would cause and increase in slurry volume of up to 200%. This increase is less pronounced but still considerable for flushing V-shaped solid floors (10–100%). Besides investment costs for the technology, the storage and application of this extra slurry volume will also lead to additional operational costs. Flushing with diluted formaldehyde solutions allows use of much less water, because the reduced urease activity is more effective than dilution or removal of urine. A disadvantage of the use of formaldehyde is a potential for the emission of formaldehyde gas to the inside air, which might have negative health effects. Safety risks could be minimised when indoor air concentrations can be related to the concentration of formaldehyde in the flushing solutions and when other relevant conditions (e.g. temperature) and limits for concentrations of formaldehyde gas in work-place environment (Ogink & Kroodsma, 1996) are taken into account.

Control of pH

Reduction of pH through slurry acidification is an effective way to reduce NH_3 emissions. Although different organic and inorganic acids could be used, experiments were only carried out using nitric acid. This was done basically from the point of view of possible substitution of additional chemical fertilisers by slurry mixed with nitric acid. However, due to the risk of denitrification of the nitrate added and consequently the emission of the environmentally harmful N_2O, pH had to be kept below 4.5. The amount of nitric acid needed to achieve that pH value leads to slurry with high nitrogen contents (e.g. around 9 g N kg^{-1}; Bleijenberg *et al.*, 1995). In order to prevent the risk of extra nitrate leaching when using acidified slurry for (grassland) fertilisation, advanced application technology for small amounts of slurry is required to match N fertilisation rates with the N demand of the grassland. Organic or other inorganic acids may be an alternative. However, no literature was found on this relative to dairy husbandry.

Housing systems

Ammonia emission per cow for tie stalls (5–27 g day^{-1}) tends to be lower then for loose housing systems with cubicles (25–45 g day^{-1}). The emission reducing effect in tie stalls is mainly caused by a reduction of surface area of the pit and the, urine and faeces fouled, floor. Drawbacks of tie stalls are generally related to a higher labour demand, especially for milking and feeding. Furthermore, new building of tie stalls will be forbidden or it is in discussion in some countries (e.g. Switzerland) from the point of view of animal welfare. In that perspective, important topics are freedom of movement for the cows and possibilities to conduct natural behaviour. These requirements are met in systems with loose housing on straw, although NH_3 emission for this type of dairy housing (one measurement) might be near cubicle house emission levels. In addition, Groenestein & Reitsma (1993) found methane emissions of approximately 1 kg day^{-1} per cow for these systems. This is substantially higher than average methane emissions from slurry based dairy cow housing systems (0.15–0.37 kg day^{-1} per cow; Crutzen *et al*., 1986; Van Der Hoek, 1984) and may be related to anoxic degradation processes in the straw bedding. An evaluation of housing systems in the framework of NH_3 emission, therefor, needs to be extended with animal welfare and other environmental aspects.

Floor systems

Compared to slatted floors, longitudinal V-shaped solid floors have a potential for a lower NH_3 emission (52%) as can be concluded from data presented in Table 2. This statement might be questioned when emission data reported for cubicle housing systems equipped with slatted (26-45 g day^{-1} per cow) and V-shaped floors (25 g day^{-1} per cow) are considered (Table 1). However, besides the small number of data present for the comparison, experimental conditions during the measurements reported in Table 1 were different. Slatted floor research was carried out in different countries, in different seasons and under different management conditions, whereas data used for the direct comparison (Table 2) were obtained from an experiment with both floor types under comparable experimental conditions. Braam *et al.* (1997) and Braam & Van Den Hoorn (1996) concluded that the design of solid floors and in particular the design and area of openings are important features when it comes to reduction of air exchange and maximisation of emission reduction. In the evaluation of the emission reducing effect of housing systems with V-shaped solid floor, compared to slatted floors, the volume of urine left upon the floor surface after each urination needs to be considered too. Urine volume and urea concentration both determine the amount of urea upon the floor and thus also the potential NH_3 production in and emission from the urine puddles upon the floor. Braam & Van Den Hoorn (1996) reported typical values for both parameters are 0.6 mm and 0.8 m^2 respectively for clean slatted floors, while for V-shaped (3% slope) solid floors due to draining of urine typical values are 0.15 mm and 1.2 m^2 respectively. This means that the potential NH_3 emission for a slatted floor is on average three times higher than for a V-shaped solid floor. Both the reduced potential emission and the reduced air exchange when using solid floors may contribute to the emission reduction reported. A major point of attention when using solid floors in general and inclined solid floors in particular is locomotion of the animals. On an inclined surface cows can easily loose grip which may cause slip incidents and injuries, especially when faeces are not removed thoroughly. Floors with sufficient floor surface texture and roughness may improve that situation (Dumelow & Albutt, 1988). Furthermore, Braam *et al*. (1997b) showed that regular wetting of the floor surface could improve faeces removal and reduce the problems mentioned before.

Synthesis

Assuming NH_3 in dairy cow buildings only originates from urinary urea and 80% of urinary N is in the form or urea, potential daily NH_3 emission per cow is 65–260 g (80% of 80–320 g N excreted in urine per cow and per day). Measurements (Table 1) have shown that the actual daily NH_3 emission is in the order of magnitude of 30 g per day, which is 12–46% of the potential emission. The lower percentage is assumed to be relevant for intensive dairy farming and related high levels of N input. An important reason for the large difference between actual and potential emission is that at pH values for urine and slurry, on average 8.5 and 7.5 respectively, only a relatively small percentage of TAN is present in the form of volatile, unionised NH_3. Even at reported pH levels of around 8.6 for urine on the floor and the top layer of slurry in the pit (Elzing & Monteny, 1997a), much of the TAN will be present as non-volatile NH_4^+. Beside pH, also other emission determining parameters have to be considered to fully explain the low actual emission relative to the potential emission. Elzing & Monteny (1997a, 1997b) found that the mass transfer parameters air velocity and temperature highly determine the maximum volatilisation rate per urination, occurring at approximately 2 h after urine has been deposited on the floor, as well as the duration of the volatilisation process (up to 15 h or more). At air velocities, temperatures and emitting surface areas found in diary cow buildings, NH_3 losses due to mass transfer (volatilisation) will be at a relatively low level when compared to NH_3 production in the liquid following urea hydrolysis. Furthermore, each urine pool upon the floor will be refreshed within 10 h at an average urination frequency per cow of 11 day^{-1} (Whitehead, 1995), a floor area of 0.8 m^2 covered by one urination, an available floor area per cow of 3.5 m^2 and random distribution of urinations over the available floor area (Monteny *et al.*, 1998). The volatilisation process of the original urine pool will therefor never run to completion.

Agricultural NH_3 emission originates for 53% and 60% from cattle husbandry in Europe and The Netherlands, respectively (Asman, 1995; Anonymous, 1996). Pig and poultry husbandry is responsible for the remainder. When Dutch emission reduction goals (70% in 2005 relative to 1980) would be applied on a European scale, NH_3 emissions from all sources (land spreading slurry, buildings, storages, grazing) would have to be substantially reduced to achieve them.

New techniques for slurry application and covering of outside slurry storages are already law enforced in The Netherlands since the late 80's. They are applied on a large scale nowadays. As a consequence, the national NH_3 emission reduction was calculated to be approximately 69 kton (34%) in 1995 compared to 1980 (Anonymous, 1996). The contribution of cattle housing and storage systems to the total NH_3 emission in The Netherlands was estimated at 45 kton in 1995 (Anonymous, 1996). Based upon the number of dairy cows relative to the number of other cattle (Anonymous, 1995), it can be assumed that approximately 80% (36 kton per year) of this amount originates from dairy cow buildings. Data presented in Table 2 show that an NH_3 emission reduction of 50% seems technically feasible. This can be achieved through innovative floor systems, flushing with diluted formaldehyde, and through a combination of feeding strategies and e.g. flushing with water.

Assuming 100% penetration of these measures in practice, maximal reduction of the NH_3 emission on a national scale will be 18 kton. This means that the contribution by dairy cow buildings to achieve the government goal in 2005 (an additional annual reduction of 74 kton from 1995 onward; total reduction of 143 kton per year) will be small and a further emission reduction from all agricultural sources will be necessary. Furthermore, annual costs on farm scale of these NH_3 emission reducing measures might be significant (Van Scheppingen *et al*., 1995), although real figures from practice are few.

Emission reduction in animal buildings generally lead to an increase in the nitrogen content of the slurry. This might imply an additional NH_3 emission during storage and land spreading. However, when measures are taken to reduce these emissions substantially (covering of storages, low emission land application), the additional emission will be low.

Conclusions

Accurate measurement of ventilation rates for naturally ventilated animal buildings has become feasible using tracer gas mass balance methods.

Data on the NH_3 emission from different types of dairy cow housing systems indicate that variation is large and that emission from tie stalls (5–27 g day^{-1} per cow) is generally lower than from loose housing systems (20–45 g day^{-1} per cow). Urea concentration in the urine, urease activity, pH, temperature, air velocity and area of emitting surfaces (floor, pit) are influencing parameters for the emission of NH_3. Measures to reduce NH_3 emission from dairy cow buildings affect one or more of these parameters. Most effective measures are flushing with formaldehyde (reduction of urease activity), introduction of V-shaped solid floors (minimising air exchange between pit and building, and reduction of air velocity in the pit), feeding strategies (lowering or urea concentration in the urine) and slurry acidification (pH control). Drawbacks of these measures, like the possible volatilisation of formaldehyde gas when flushing floors with diluted formaldehyde, danger of slipping of the cows on V-shaped solid floors and risks of unwanted emissions of methane (straw systems) and nitrous oxide (acidification with nitric acid) will have to be addressed to ensure application in practice. For the Netherlands, maximal emission reduction through implementation of reducing measures in dairy cow buildings is estimated at 18 kton of NH_3 per year.

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