ÉMISSIONS D'AMMONIAC EN PROVENANCE DES INFRASTRUCTURES AGRICOLES

Mémoire de maîtrise en environnement (volet recherche)

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ABSTRACT

Gaseous ammonia emissions from livestock production are a well known source of anthropogenic ammonia emissions and have been the subject of numerous studies in Western Europe and in the United States of America. They are deemed responsible for the acidification of ecosystems. Furthermore, ammonia emissions from intensive livestock operations located in the vicinity of major cities induce favourable conditions for smog formation. Ammonia volatilization from manure also reduces its effectiveness as a fertilizer by reducing its nitrogen content, an important nutrient for plant growth. Certain technologies and structures exist to cover manure storage tanks in order to limit these ammonia losses to the atmosphere. Very few studies have been done in Canada where climate and manure management practices differ widely from those in Western Europe and in the United States of America. In this project, a measurement campaign was financed by Agriculture and Agrifood Canada on four commercial livestock production infrastructure to begin the development of national ammonia inventory.

Commercial dairy and swine manure storages covered by floating geomembranes were monitored for periods exceeding six months in the Eastern Townships of Quebec. The swine manure storage emitted negligible amounts of ammonia, from $5.9 \times 10^{-3}$ to $0.14 \, \mu g \cdot m^{-2} \cdot s^{-1}$ over the summer time. The dairy manure storage emitted more substantial amounts of ammonia when the manure surface was frozen in winter, from 1.9 to 16 $\mu g \cdot m^{-2} \cdot s^{-1}$, then when unfrozen, 93 to 166 $\mu g \cdot m^{-2} \cdot s^{-1}$. A structural difference in the covering technology at the dairy manure storage rendered it less airtight than the swine manure storage. Therefore, the efficiency of a cover to limit ammonia emissions from manure is function of its air tightness. Ammonia emission rates from two tie-stall commercial dairy buildings were also monitored in the Eastern Townships of Quebec. Ammonia emission measurements done at building A during winter 2007 ranged from 3.77 to 6.80 $g \cdot day^{-1} \cdot animal^{-1}$ while those performed at building B during summer 2007 were higher and ranged from 11.33 to 18.20 $g \cdot day^{-1} \cdot animal^{-1}$. These values fall within the wide range of those published for Western Europe and the United States of America. However, unlike studies completed in Europe using similar procedures, the methods used to measure gaseous ammonia concentrations and building ventilation flow rates in this study were validated in controlled environments.

KEY WORDS

Ammonia, Agriculture, Gaseous Emission, Dairy housing, Manure storage, Geomembrane, Ventilation
RÉSUMÉ

Les productions d'élevage constituent la principale source d'émissions anthropiques d'ammoniac gazeux. Ces émissions sont responsables de l'acidification de plusieurs écosystèmes terrestres et aquatiques. De plus, les émissions d'ammoniac de productions d'élevage situées près des villes peuvent induire des conditions favorables à la formation de smog. La volatilisation de l'ammoniac du lisier peut réduire la valeur fertilisante du lisier en diminuant sa teneur en azote, un nutriment essentiel pour la croissance des plantes. Certaines technologies de recouvrement des fosses existent afin de réduire ces pertes en azote. Les émissions ont fait l'objet de plusieurs études en Europe de l'Ouest et aux États-Unis d'Amérique. Par contre, très peu d'études ont été faites au Canada alors que nos pratiques de gestion des lisiers et notre climat diffèrent largement de ces derniers. Une campagne de mesure sur quatre infrastructures d'élevage canadiennes a été financée par Agriculture et Agro-Alimentaire Canada dans le but de commencer à bâtir un inventaire national canadien pour l'ammoniac.

Des fosses commerciales dans la région de l'Estrie recouvertes de géotextile, l'une contenant du lisier de porc et l'autre du lisier de bovin laitier, ont été suivies pour des périodes supérieures à six mois. La fosse de lisier de porc a émis des quantités négligeables d'ammoniac dans l'atmosphère pendant l'été. Les émissions d'ammoniac du lisier de bovin laitier gelé étaient entre 1.9 et 16 μg·m⁻²·s⁻¹ et étaient nettement supérieures sur le lisier dégelé, soit 93 à 166 μg·m⁻²·s⁻¹. La structure recouvrant la fosse de lisier de bovin laitier était moins étanche que celle recouvrant la fosse de lisier de porc. Donc l'efficacité d'une technologie de recouvrement d'une fosse à réduire les émissions d'ammoniac est fonction de son étanchéité. Les émissions d'ammoniac de bâtiments d'élevages laitiers ont aussi été suivies lors de cette étude. Le bâtiment A émettait en hiver 2007 entre 3.77 et 6.80 g·jour⁻¹·animal⁻¹ d'ammoniac alors que le bâtiment B en émettait plus à l'été 2007, soit entre 11.33 et 18.20 g·jour⁻¹·animal⁻¹. Ces mesures se comparent à celles retrouvées dans la revue scientifique pour l'Europe et les États-Unis, qui se caractérisent par une grande variabilité. Les méthodes utilisées lors de cette étude pour mesurer les taux d'émissions d'ammoniac des bâtiments étaient similaires à celles utilisées en Europe. Or, à l'instar des études européennes, la précision des équipements utilisés pour mesurer les taux de ventilation et les concentrations d'ammoniac dans cette étude ont été évalués en milieu contrôlé.

MOTS CLÉS

Ammoniaque, Agriculture, Émissions gazeux, Bâtiments d'élevage, Fosses à lisier, Géomembranes, Ventilation
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CHAPTER 1

INTRODUCTION

1.1 Nature and scope of the problem

Ammonia emissions in the atmosphere are known to have many adverse effects on the environment. Indeed, ammonia can react with nitrates and sulfates to produce ammonium nitrate and ammonium sulphates, molecules responsible for the formation of particulate matter less than 2.5 μm in diameter (PM$_{2.5}$) and in turn smog [Cadle, 1972]. Furthermore, these molecules can travel great distances in the atmosphere prior to deposition in aquatic and terrestrial ecosystems, causing their acidification and loss of biodiversity [Bobbink et al., 1998; Erisman et al., 2000; Grennfelt et al., 1986]. Ammonia is also known to cause chronic lung diseases in humans frequently exposed to concentrations exceeding 25 ppm [Règlement sur la qualité du milieu de travail S-2.1 R.15, 2008].

Several activities allow ammonia inputs into the environment. Rhizobia living in symbiotic relationships with legume plants can fix atmospheric nitrogen into ammonia, a readily usable form for the plant. Ammonia can also be mass-produced by the Haber-Bosch combustion process in industrial applications [Sutton et al., 2008]. Indeed, ammonia is used as a refrigerant due to its high latent heat of vaporization and it is also the main component in inorganic fertilizer, which warrants the mass production of ammonia [Sutton et al., 2008]. Ammonia is also a secondary pollutant of catalytic converter systems in gasoline engines [Heeb et al., 2008]. However, the process that contributes the most to ammonia inputs in ecosystems is ammonification [Aneja et al., 2001]. Certain bacteria and fungi can decompose organic nitrogen into ammonium ions. This reaction is catalysed by ureases enzymes which are commonly found in soils and feces [Rotz, 2004]. This phenomena can also occur in concentrated feces and urine mixtures where urine provides readily hydrolisable urea and feces provide urease enzymes. This is why animal manure is the greatest contributor of gaseous ammonia emissions. This is observed in figure 1.1 which shows the relative contribution of several ammonia emission sources.

Livestock production is deemed to be the greatest contributor of anthropogenic ammonia emissions in Europe and Canada [ECETOC, 1994; Kurvits et al., 1998]. The european community has studied extensively ammonia emissions as a result of high acidification levels of their terrestrial and aquatic ecosystems located in zones with a high density of livestock productions. Several policies are already in place to con-
control ammonia emissions in Europe [Erisman et al., 2008]. Certain legislations even provides for national emission ceilings to limit ammonia emissions, the greatest reductions being reported for the Netherlands, Denmark and the UK [Amann et al., 2000]. The goals fixed by the Gothenburg convention on long-range transboundary air pollution and the National Emission Ceilings Directive is expected to cost European countries two billion USD each year in administration fees and research & development [Hutchings et al., 2001].

Denmark is one of the rare countries able to establish ammonia emission factors typical of their agricultural practices because of the great number of studies performed in the country. Great variability in ammonia emission rates for either similar livestock production, manure handling practices or housing types was demonstrated through the exhaustive number of studies performed in Denmark [Hutchings et al., 2001]. This shows the necessity of elaborating emission factors specific to a given country by direct emission measurements.

Extensive information on ammonia emission levels for different livestock productions are necessary for establishing accurate ammonia emission inventories and in
Ammonia volatilization from manure also reduces its fertilizer value. This nitrogen loss increases farming operation costs by the additional purchase of inorganic fertilizer.

In the United States, studies on ammonia have increased due to concern over loss of biodiversity and the health and well-being of farmers and their neighbours due to chronic and acute ammonia inhalation from livestock productions [Gay et al., 2003]. The animal industry in the USA is currently funding a 2-year large-scale measurement program to characterize ammonia emissions from swine, dairy and poultry operations in several areas in the USA. The American Environmental Protection Agency (EPA) is providing guidance for this program, the National Air Emissions Monitoring Study [Aneja et al., 2007]. An emission factor for ammonia is representative for a specific time period (season, month, etc.) and attempts to relate the quantity of ammonia emitted with an activity associated with its release: manure storage, treatment, handling or spreading. Emission factors typical of livestock productions are commonly expressed in the following units: kg NH$_3$·animal$^{-1}$·year$^{-1}$, kg NH$_3$·AU$^{-1}$·month$^{-1}$, kg NH$_3$·m$^{-3}$ of manure per day, kg NH$_3$ per ton of manure per month, μg NH$_3$·m$^{-2}$·s$^{-1}$, kg NH$_3$·m$^{-2}$ of floor or manure surface per day. Ammonia emission factors currently used in Canada have not been derived from Canadian studies [Kurvits et al., 1998].

1.2 Objectives

The object of this master project is to establish ammonia emission factors from livestock buildings and manure storages in Canada. This will increase the accuracy of the Canadian ammonia inventory. Also, new technologies are available on the market to limit nitrogen losses from manure storages such as geomembrane covers. The commercial manure storages studied were covered by geomembranes and located in Compton and St-François-Xavier-de-Brompton; both towns located in the Eastern Townships county in the Province of Quebec. The storage in Compton contained dairy manure while the other in St-François-Xavier-de-Brompton contained swine manure. Two tie-stall commercial dairy barns in the same county were also retained for this study. Building A was located in Cookshire while building B was in Compton. The following tasks were completed:

- Modify existing measurement systems installed on livestock infrastructures for ammonia measurements;
- Evaluate performance and precision of equipment used for ammonia concentration and building ventilation rate measurements;
- Measure ammonia emission rates from two dairy livestock buildings, one swine manure storage and one dairy manure storage;
- Measure environmental parameters and manure physico-chemical characteristics that can influence ammonia emission rates;

- Compare measured ammonia emission rates to those reported in the literature in relation to measured environmental and manure physico-chemical characteristics.

Two scientific articles describing these tasks have been submitted to peer-reviewed journals. The article entitled *Ammonia Emission Rates from Covered Concrete Manure Tanks in Eastern Canada*, accepted for publication in Transactions of the American Society of Agricultural and Biosystems Engineers (ASABE), is presented in chapter 4. The article entitled *Ammonia Emission Rates from Dairy Livestock Buildings in Eastern Canada*, submitted to Biosystems Engineering, is presented in chapter 5.

### 1.3 Documentation source

The main subject matter of this study is relevant to disciplines related to agricultural and bioressources engineering. Therefore, most of the documentation that was consulted consisted of published articles in peer reviewed journals in this field:

- American Society of Agricultural and Biosystems Engineers (ASABE) affiliated journals;

- The Institution of Agricultural Engineers (IAgrE) official publication, Biosystems Engineering, formerly known as the Journal of Agricultural Engineering Research;

- Several other journals related to air quality such as Atmospheric Environment, Environmental Pollution;


The Canadian Society of Agricultural and Biosystems Engineers also has an official publication but no commercial scale study such as this one has been completed in Canada. This is why most of the documentation found was relevant to American and European studies. The acquirement of such documentation was possible via the databases of Agriculture & Agrifood Canada.

### Chapter bibliography


CHAPTER 2
LITERATURE REVIEW

2.1 Physico-chemistry of ammonia volatilization

Ammonia emissions from manure are prone to high spatial and temporal variability due to the large number of factors involved in its volatilization. This affects the development of representative emission factors [Aneja et al., 2007]. The following environmental and manure physicochemical parameters affect ammonia volatilization rates from livestock production infrastructures:

- Air temperature and air speed just over the manure surface [Kroodsma et al., 1993; Ni, 1999];
- Ionic charge, ammonia concentration, pH and temperature of manure [Ni, 1999; Arogo et al., 2003; Hafner et al., 2006].

These physico-chemical parameters are influenced by livestock production and manure management practices [Rotz, 2004]. These management parameters are listed in Table 2.1.

Table 2.1: LIVESTOCK PRODUCTION MANAGEMENT PRACTICES AFFECTING TO AMMONIA EMISSIONS

<table>
<thead>
<tr>
<th>Livestock management</th>
<th>Milking schedules [Kroodsma et al., 1993]</th>
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<tr>
<td></td>
<td>Diet composition [Rotz, 2004]</td>
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<td></td>
<td>Water consumption [Rotz, 2004]</td>
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<td>Livestock housing management</td>
<td>Ventilation flow rates [Kroodsma et al., 1993]</td>
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<td></td>
<td>Air Temperature [Kroodsma et al., 1993]</td>
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<tr>
<td>Manure management</td>
<td>Type of manure handling systems [Swierstra et al., 2001; Misselbrook et al., 1998; Kroodsma et al., 1993]</td>
</tr>
<tr>
<td></td>
<td>Scraping method and frequency [Rotz, 2004]</td>
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<td></td>
<td>Type of litter used [Amon et al., 2001; Rotz, 2004]</td>
</tr>
<tr>
<td></td>
<td>Type of manure storage structure [Gay et al., 2003]</td>
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<tr>
<td></td>
<td>Ambiant conditions in manure storage [Ni, 1999]</td>
</tr>
</tbody>
</table>

Total ammonia (ammonia and ammonium) in manure available for volatilization depends on livestock nutrition. Livestock animals typically use less than 30% of the nitrogen they ingest, which leaves 50 to 80% to be excreted in urine and 20 to 30% in feces. Variations depend on animal species or its life stage. Urea is the source of 97% of all nitrogen contained in urine [McCrary et al., 2001]. Transformation of urea into ammonium ions is dictated by ureic activity where urease enzymes contained in feces
can readily decompose the urea in urine. Several studies evaluated the reduction in ammonia emission rates from dairy barns by limiting contact between feces and urine such as using grooved floors for manure handling [Braam et al., 1999; Kroodsma et al., 1993; Messelbrook et al., 1998; Swierstra et al., 2001]. Housing animals over sloped grooved floors allows for urine to drain towards a collector while feces remain on the floor separate from the urine. Furthermore, ureic activity increases exponentially with increasing manure temperature. Complete conversion of urea into ammonium can occur in dairy buildings only within a few hours depending on indoor temperature and manure handling conditions. Ureic activity becomes negligible at temperatures below 10°C [Rotz, 2004].

Ammonia present in feces as proteins can also be hydrolysed into peptides and amino acids and then deaminated into ammonia by proteolitic bacteria. This process of fecal ammonia mineralisation is done over periods of several months, therefore at a much slower rate than urea decomposition. Fecal ammonia mineralisation is considered insignificant during short-term manure storage [McCrory et al., 2001] but can become the dominant mode of ammonia volatilization for long-term storage over several months at warm temperatures [Rotz, 2004].

Once organic nitrogen is transformed into ammonium, the conversion of ammonium into gaseous ammonia in solution is a chemical equilibrium process dependent on pH, temperature and total ammonia concentration. Ammonia is a weak base that can react with water to produce its conjugate acid, ammonium, and hydroxide ions. The reverse reaction can also occur as shown in equation 2.1.

\[ NH_3(aq) + H_2O(l) = NH_4^+(aq) + OH^-(aq) \]  

(2.1)

Higher pH or temperatures make the equation favor gaseous ammonia relative to ammonium [Snoeyink et al., 1980; Loehr, 1984]. The equilibrium constant that controls the reaction is the dissociation constant for ammonium, \( K_d \). At 25°C in an aqueous solution of ammonia in water, this constant is \( 5.6 \cdot 10^{-10} \). At a pH above 9.3, \( (pK_d = -logK_d) \), ammonium ions will not be present in solution. The reverse reaction where an ammonium ion releases a proton to ammonia can also occur. The equilibrium constant controlling the latter is the alcalinity constant of ammonia, \( K_b \). At 25°C in distilled water, this constant is \( 1.8 \cdot 10^{-5} \). For a pH below 4.7 \( (pK_b = -logK_b) \), gaseous ammonia in solution would be absent [Snoeyink et al., 1980]. Both constants are related to each other by the equation \( K_d \times K_b = K_W = 10^{-14} \) at 25°C , or \( pK_d + pK_b = 14 \) according to logarithmic algebra. As for ammonia dissociation constants in manure, literature reviews shows the state of confusion in its experimental determination [Arogo et al., 2003; Hafner et al., 2006].
Lastly, the transfer of dissolved gaseous ammonia in manure towards ambient air is a chemical diffusion process through a liquid-gaz interface. Ammonia is highly volatile due to its low vapour pressure at ambient temperatures. When ammonia is drawn away from the manure surface by an ammonia-free air stream blowing over it, ammonia's partial pressure in air near the manure surface drops. This in turn stimulates subsequent convective ammonia transfer from the surface of the manure to ambient air. Therefore, the rate of ammonia desorption is highly dependent on environmental conditions such as the speed and temperature of the air-stream blowing over the manure surface [Arogo et al., 1996; Ni, 1999]. One of the most popular theories to describe ammonia diffusion through the surface of manure is the two-film theory based on Henry’s law [Arogo et al., 1996; Ni, 1999]. The ammonia mass transfer rate at the manure-air interface depends on the mass transfer rate through each individual film on each side of the interface, while it is assumed that no resistance is offered through the interface itself. The two-film theory implies that three steps occur during the ammonia mass transfer from the manure surface to the atmosphere. There is the convective transfer of ammonia from the air film at the manure-air interface towards the ambient atmosphere. This provokes a concentration gradient encouraging the diffusion of ammonia through both films, and in turn through the vertical manure profile, and such following Fick’s Law of diffusion. These three steps complexify the volatilisation model for ammonia from manure [Ni, 1999]. An exhaustive review on mass transfer coefficients done by Ni [1999] demonstrated the confusion surrounding the application of developed equations for ammonia. Even though the great variability of ammonia mass transfer coefficients from manure surfaces, $11.7 \cdot 10^{-3}$ to $1.3 \cdot 10^{-6}$ m/s, they are positively related to higher wind velocities and warmer temperatures. Furthermore, greater is the liquid-gaz interface, greater is ammonia volatilization from a given infrastructure. In this respect geometry of manure storages can have an effect on ammonia volatilization rates for a given site.

2.2 Methods

2.2.1 Ammonia concentration measurements in air

Several equipments are available to measure ammonia concentrations from a stream of air [Alex et al., 2003; Phillips et al., 2001]:

- Non-dispersive infrared analyzers;
- Chemiluminescence;
- Electrochemical cells;
- Acid traps;
- Colorimetric tubes.

From this non-exhaustive list, the first three can be used for continuous measurements since a digital or analogue signal can be produced and recorded. The two last methods provide an average ammonia concentration measurement during the whole sampling period. A detailed description of infrared analyzers, acid traps and electrochemical cells will be given in the following paragraphs since these equipments are available for this study.

A non-dispersive infrared analyzer comprises of a source emitting radiation between 2.5 and 25 μm in wavelength, an absorption chamber and a radiation detector. Gas concentration measurement for a given gas is related to its characteristic amount of absorbed radiation over a characteristic spectrum. These instruments are best suited to detect a given gas within a mixture of several non homonuclear gases. With advances in narrow band optical filters, photo-acoustic techniques and automatic compensation for water vapour and carbon dioxide, non dispersive infrared analyzers now have a detection limit of 0.2 ppm for ammonia [Phillips et al., 2001]. This equipment's advantage is its robustness. They can be used over long periods of time without maintenance. However, they are prone to deterioration when in contact with dust and condensation. Therefore air streams to be analysed may require conditioning. Since ammonia is a highly reactive gas, dust filtering before analysis may cause under-estimations in ammonia content measurements for a given air stream. Similarly, ammonia can dissolve easily in condensed water vapour in the sampling tubing. Heber et al. [2001] pointed out the importance of maintaining the air sampling tubing approximately 3 °C warmer than the air samples so to avoid condensation within the lines and of changing dust filters regularly to limit dust accumulation within the sampling system.

Ammonia concentration can also be determined in the field by having an air stream sample pass through an acid solution at a measured flow rate over a recorded time period. The acid solution can then be analysed in the laboratory for total ammonia concentrations by several methods: colorimetric tubes, selective diodes or by titration. The advantages of this method is that it is precise, cheap and accounts for adsorbed dust and dissolved water vapour. However, as specified earlier, this method can only yield the average concentration over the sampling period and is labour-intensive. To obtain representative measurements of ammonia concentrations in livestock buildings and manure storages, long sampling periods are required.

Electrochemical cells are one of the most common methods to detect ammonia levels in air. They do not function well in cold temperatures and the detector often needs to be replaced [Alex et al., 2003]. Electrochemical cells consist of two or three electrodes
in an electrolyte solution consisting of electrochemically active reagents. The ammonia concentration in air is obtained by measuring the electric potential or current produced by the rate of ammonia passing through a membrane into the electrolyte filled cell. These modules are highly sensitive to sudden rises in ammonia levels and typically measure ammonia level exceeding 5 ppm [Phillips et al., 2001]. This high sensitivity to sudden rises makes them useful for detector alarms.

2.2.2 Ammonia reactivity

The high reactivity of ammonia can cause errors when measuring ammonia concentrations in air streams. The solubility of ammonia gas in water is highly dependent on temperature. One volume of water at 0 °C can dissolve 1200 volumes of gaseous ammonia while 700 volumes are dissolved at 25°C [Rose, 2004]. The chemical structure of ammonia, presented in figure 2.1, has a role in making it highly reactive. Hydrogen atoms form the base of the pyramid and are linked to the nitrogen atom by polar covalent bonds. The high electronegativity of nitrogen compared to hydrogen and its position at the apex of the pyramid creates a dipole moment. This is why ammonia can be highly adsorbant to several polymers, even teflon. Rose [2004] suggested that several studies regarding indoor air ammonia concentration measurements do not evaluate ammonia adsorptivity of gas sampling systems. After completing several controlled laboratory experiments, Rose [2004] found that ammonia adsorbed at a higher rate to low density polyethylene tubing than to teflon, but ammonia adsorption still occurred in teflon tubing at rates ranging between 2.2 and 51%.

Figure 2.1 Chemical structure of ammonia [Rose, 2004]
Apart from polymers, gaseous ammonia can potentially adsorb to dust. Reynolds et al. [1998] compared several ammonia concentration measurement methods to evaluate those able to distinguish between gaseous ammonia and dust adsorbed ammonia. Filters were installed in-line with acid traps where the air stream to be analysed was conveyed. Filters were rinsed with an acid solution to measure ammonia adsorbed to dust. Comparing ammonia concentrations from both sources, adsorbed ammonia to dust may represent between 15 and 23% of total ammonia in the air sample.

Another study by Takai et al. [2002] suggests also that prefiltration of dust induces significant differences in the ammonia content measured in an air sample:

"The ammonia contents in inhalable dust varied from about 1 to 6 \( \mu \text{g NH}_3 \) per mg of dust (1,000 to 6,000 ppm), while a content of about 7 \( \mu \text{g NH}_3 \) per mg of dust (7,000 ppm) was found in respirable dust. These concentrations were from 100 to 1000 times higher than the typical aerial ammonia concentrations in livestock buildings. Filtration of dust from the air before gas analysis or odor measurement is commonly practiced. However, the high ammonia contents seen in this study suggest that this process of dust filtration will cause not-negligible measuring error."

Considering dust concentrations measured by Takai et al. [2002] in livestock buildings ranging between 0.02 and 2.50 mg \( \cdot \) m\(^{-3}\), concentrations of ammonia adsorbed to dust range from \( 1.3 \times 10^{-3} \) to \( 6.4 \times 10^{-3} \) ppm. This fraction associated with dust is negligible relative to the gaseous fraction of ammonia contained in the air samples which varies between 3 and 35 ppm. The conflicting results of the studies performed by Takai et al. [2002] and Reynolds et al. [1998] indicate the need for subsequent studies on the matter.

2.2.3 Ammonia emissions from buildings

The mass balance approach is often used to measure emission rates from a building [Kinsman et al., 1995]. To do so, ventilation flow rates and ammonia concentrations are measured at the inlets and outlets of the building. Two different approaches are commonly used to measure ventilation rates [Phillips et al., 2001]:

- Injection of tracer gas;
- Sommation of air flows through all openings in the building.

The first method consists of injecting a tracer gas in the building at a known flowrate, and measuring its concentration at several locations upstream and downstream of the source. Ventilation rates are then approximated. This approach assumes that air is
perfectly mixed within the building. This is the greatest source of imprecision for this method [Phillips et al., 2001].

The other method of summing airflows at all openings can be done with anemometers or differential pressure sensors. Indeed, near atmospheric pressure, air can be considered an incompressible fluid following Bernoulli’s equations. Knowing the discharge coefficient of an opening and measuring the pressure differential across the opening, perpendicular air flow rates can be determined. However, perfectly perpendicular air movements are rare in naturally-ventilated buildings [Phillips et al., 2001; Potter et al., 1997]. For the case of mechanically ventilated buildings, performance curves relating air flows to pressure differentials are often available for fans from the manufacturer. However, insertion effects and mechanical wear alter the shape of this curve in the field. A way to get around this is to install anemometers permanently on fans or natural ventilation openings. Numeric integration of the velocity profiles across the opening surface would yield a ventilation rate measurement. An anemometer measuring the average air velocity across the opening can also be used [Potter et al., 1997; Phillips et al., 2001]. Several types of anemometers are available on the market: thermal, acoustic or mechanical-propeller [Potter et al., 1997]. Acoustic and thermal anemometers are very precise in clean environments but are prone to malfunction in dusty environments such as livestock buildings. Mechanical propeller type anemometers are more robust but are more labour-intensive since they may require to be assembled and calibrated for specific applications to yield precise ventilation measurements.

2.2.4 Ammonia emissions from manure storages

The following methods to measure ammonia emission rates from manure storages are commonly used in the literature:

- nitrogen mass balance;
- ammonia flux from surfaces covered by an apparatus.

A pilot-scale study on nitrogen losses from manure storages completed in Canada used the nitrogen balance method [Patni et al., 1991]. Variations in nitrogen concentrations in the manure itself recorded over time can be used to approximate indirectly ammonia emissions. However, successions of nitification and denitrification cycles can induce N₂O emissions instead of ammonia emissions and this method can not differentiate between these two nitrogen losses. Also, this method is labour-intensive because of the great number of manure samples to handle to account for ammonia and nitrogen concentration spatial variations in the manure storage.
Several apparatus have been built to determine ammonia flux from a given surface. By placing the apparatus over a surface, measuring variations in ammonia concentrations of the air evacuated and the ventilation flowrate through the apparatus, a mass balance can be completed for that surface. Several variations of such apparatus have been described in the literature. Different sensors can be used to measure ventilation rates and several air sampling systems can be associated to measure ammonia concentrations. Both of the former have been described in preceding sections. At small scale, these apparatus can be used to repeat several times the same experiments to evaluate the effect of different treatments. Gay et al. [2003] for instance wanted to generate a database for future research and used this method to measure ammonia emission rates from several manure storages. The apparatus used only covered a surface area of 0.23 m$^2$, causing great variability in ammonia emission rates. Spatial variability in ammonia emission rates over a given manure storage surface area can be caused by several factors such as environmental conditions (sunlight and wind profiles) and fresh manure inlet location where total ammonia concentrations in the manure may be higher. Therefore, to measure ammonia emission rates representative of a given manure storage and climate, apparatus covering the totality of the manure storage must be used [Amon et al., 2001]. Such technologies are now available on the market in order to limit nitrogen losses from manure. For instance, covering a manure storage with an air-tight geomembrane, installing an evacuation duct mounted with an anemometer or flowmeter and allowing for gas to be sampled regularly can provide a means to evaluate their performance for reducing ammonia volatilization.

2.3 Reported ammonia emission factors

Ammonia emission rates from livestock operations have been reported in the literature for several countries. Even though most of them come from countries with different climates, livestock and manure management practices than those found in Canada, an exhaustive review of these studies are presented in this section.

2.3.1 Dairy livestock buildings

None of the studies on dairy livestock buildings presented in tables 2.2 and 2.3 attempted to establish the precision of the methods and equipments used even though ammonia emission rates vary greatly between studies. For instance, Groot Koerkamp et al. [1998] published emission factors ranging from 314 mg · h$^{-1}$ · animal$^{-1}$ to 1245 mg · h$^{-1}$ · animal$^{-1}$ in dairy housing buildings when using an identical quantification methodology for all buildings.
Table 2.2: METHOD DESCRIPTIONS USED FOR DAIRY LIVESTOCK BUILDING STUDIES

<table>
<thead>
<tr>
<th>Study</th>
<th>Building and method description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kroodsma et al. [1993]</td>
<td>Closed chamber approach was used continuously from January to June on a mechanically ventilated building. Ammonia concentration was measured with a chemiluminescent analyser.</td>
</tr>
<tr>
<td>Groot Koerkamp et al. [1998]</td>
<td>Closed chamber approach was used continuously from January to June on a mechanically ventilated building using straw as bedding material, including free-stall and tie-stall buildings, therefore excluding slatted floor buildings where manure is stored underneath floor. Ammonia concentration was measured with a chemiluminescent analyser.</td>
</tr>
<tr>
<td>Demmers et al. [2001]</td>
<td>Trace gas method was used to measure ventilation rates from a naturally ventilated building with cubicles. The manure was handled by scraping the floors. Ammonia emission rates were measured continuously for 5 months. The method was validated by releasing a known quantity of gas into the building while empty (recovery rate of 108%). They demonstrated that knowledge on discharge coefficients lacked in order to properly use differential pressure measurements on air inlets and outlets of naturally ventilated buildings in order to determine their ventilation flow rates. Ammonia concentration was measured with a chemiluminescent analyser.</td>
</tr>
<tr>
<td>Amon et al. [2001]</td>
<td>Closed chamber approach was used for numerous 24-hour periods over the course of a year on a tie-stall barn containing 12 cows. A pre-calibrated anemometer was apposed to the only central exhaust fan of the building. Straw was used as bedding material and manure was mugged out twice a day. Micro-meteorological methods were used.</td>
</tr>
<tr>
<td>Gay et al. [2003]</td>
<td>Data was obtained by collecting air samples in Tedlar® bags while building flow rates were estimated by measuring pressure difference across the fan and correlating them to flowrates obtained from the fans manufacturer's calibration curves. Ammonia concentration was determined with colorimetric tubes or acid traps.</td>
</tr>
<tr>
<td>Zhu et al. [2000]</td>
<td>Air samples were collected in Tedlar® bags for 2 hour periods over a total of 12 hours (7am to 7 pm) in a naturally ventilated building where air flow rates were measured using CO2 balances. Ammonia concentration was measured with colorimetric tubes.</td>
</tr>
<tr>
<td>Rose [2004]</td>
<td>Emission factors were derived from an emission flux chamber apposed over one stall for several hours at a time. Ammonia concentration was measured with a chemiluminescent analyser.</td>
</tr>
</tbody>
</table>

1 The length of the experiments was not specified in the study.

There is also a high temporal variability of ammonia emissions rates, demonstrating the relevance of regular air sampling over long time intervals [Amon et al., 2001; Heber et al., 2001]. In the Kroodsma et al. [1993] study for example, daily ammonia emission...
rate profiles from a livestock building fluctuated up to 25% on a given day. In another study not described in tables 2.2 and 2.3, Harper et al. [2004] measured ammonia emission rates from a dairy livestock building during the daytime period and reported divergent emission rates to those done over a 24-hour period in the same building. Daytime period ammonia emission rate was on average 2.57 kg/animal-year while it was 3.36 kg/animal-year for the 24-hour period.

Studies by [Gay et al., 2003], [Zhu et al., 2000] and [Rose, 2004] presented in tables 2.2 and 2.3 attempted to extrapolate ammonia volatilisation rates from a small surface to complete buildings. The number of animals housed in these buildings were for the most part unknown. Rose [2004] suggested from analysis of his results that a great spatial variability in ammonia emission rates existed within a building making it difficult to extrapolate measurements obtained from a small surface to the whole building. Indeed, because of high variations in temperatures, wind speeds near humid surfaces within the building, the ammonia flux from an area ranging between 0.1 and 1 m² in size under a chamber can not properly represent the ammonia emission rate for the whole building [Kroodsma et al., 1993; Meisinger et al., 2001].

Table 2.3: AMMONIA EMISSION FACTORS FOR DAIRY LIVESTOCK BUILDINGS

<table>
<thead>
<tr>
<th>Study</th>
<th>Country</th>
<th>Season</th>
<th>Emission Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kroodsma et al. [1993]</td>
<td>Netherlands</td>
<td>January to June</td>
<td>38.5 to 60.2 kg/month</td>
</tr>
<tr>
<td>Groot Koerkamp et al. [1998]</td>
<td>Denmark</td>
<td>Winter</td>
<td>560 mg · h⁻¹ · animal⁻¹</td>
</tr>
<tr>
<td></td>
<td>Netherlands</td>
<td>Winter</td>
<td>974 mg · h⁻¹ · animal⁻¹</td>
</tr>
<tr>
<td></td>
<td>England</td>
<td>Winter and Summer</td>
<td>314 mg · h⁻¹ · animal⁻¹</td>
</tr>
<tr>
<td></td>
<td>Germany</td>
<td>Winter and Summer</td>
<td>538 mg · h⁻¹ · animal⁻¹</td>
</tr>
<tr>
<td>Demmers et al. [2001]</td>
<td>England</td>
<td>February to May</td>
<td>8.9 kg/AU-190 days</td>
</tr>
<tr>
<td>Amon et al. [2001]</td>
<td>Austria (Alps)</td>
<td>Winter and Summer</td>
<td>3.9 to 7.4 g · day⁻¹ · AU⁻¹</td>
</tr>
<tr>
<td>Gay et al. [2003]</td>
<td>USA (Minnesota)</td>
<td>All Seasons</td>
<td>0.64 to 196 µg · m⁻² · s⁻¹ (43.1 ± 46.2 µg · m⁻² · s⁻¹)³</td>
</tr>
<tr>
<td>Rose [2004]</td>
<td>USA (Texas)</td>
<td>Summer</td>
<td>3.2 µg · m⁻² · s⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Winter</td>
<td>11 µg · m⁻² · s⁻¹</td>
</tr>
</tbody>
</table>

³ Mean ± standard deviation

2.3.2 Manure storages

Certain technologies have been developed to reduce ammonia losses from manure storages by limiting the surface exposed to ambient air. Floating covers made out of natural or man-made materials (plastic, straw, oil) have been shown to reduce ammonia losses from 80 to 95 % [Rotz, 2004; Xue et al., 1999]. Permanent lids can
nearly eliminate ammonia storage losses when an appropriate seal is provided [Sommer et al., 1993]. Amon et al. [2006] showed for exterior pilot-scale concrete dairy manure storages in the Austrian Alps that a wooden lid reduced ammonia emission rates by 28% and 45% respectively during winter and summer conditions. Converting reported data from the Amon et al. [2006] study, ammonia emissions from the covered tanks ranged from 10 to 17 μg·m⁻²·s⁻¹. Approximately 10 metric tons of manure was stored in each storage for periods of 100 to 140 days. Of the available studies on atmospheric ammonia emissions from agriculture in Western Europe, the Austrian Alps climate is the most similar to Canada’s climate.

Tables 2.4 and 2.5 describe methods and results obtained in studies completed on dairy and swine manure storages. Geographically, the nearest extensive study to Eastern Canada on direct measurements of ammonia emission rates from manure storage found in the literature was in the state of Minnesota in the United States of America [Gay et al., 2003]. However, the measurements were taken over such different temporal and spatial scales that they are inapplicable for deriving Canadian emission factors. Furthermore, ammonia emission rate measurements in Minnesota showed great variations.

Table 2.4: METHOD DESCRIPTIONS USED FOR MANURE STORAGE STUDIES

<table>
<thead>
<tr>
<th>Study</th>
<th>Manure and method description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gay et al. [2003]</td>
<td>Measurements using a portable wind-tunnel covering 0.23 m² of manure surface contained in concrete tanks. The ultimate goal was to build an ammonia emission database for the state of Minnesota.</td>
</tr>
<tr>
<td>Zahn et al. [2001]</td>
<td>Over a dozen manure storages in Iowa were studied, ranging from concrete-lined basins to lagoons. Micrometeorology modelling was used for 24-hour periods while air samples were drawn thru acid traps. Surface areas of the manure storages studied were not specified.</td>
</tr>
<tr>
<td>Patni et al. [1991]</td>
<td>Ammonia loss from airtight covered manure tanks was determined by following changes in total nitrogen and ammonia concentrations of the manure at several locations in the tanks over several weeks.</td>
</tr>
<tr>
<td>Amon et al. [2006]</td>
<td>Ammonia emissions of each treatment (with and without wooden lid) were measured at least twice a week for several hours using an open dynamic chamber. The concrete circular tanks contained 10 m³ of dairy manure each and measured 2.5 m in diameter. Storage periods were 100 days in winter and 140 days in summer. Mean net total emission measurement periods were 450 h per treatment.</td>
</tr>
</tbody>
</table>
Table 2.5: EMISSION FACTORS FOR MANURE STORAGE

<table>
<thead>
<tr>
<th>Study</th>
<th>Country</th>
<th>Season</th>
<th>Livestock</th>
<th>Manure Characteristics</th>
<th>Emission factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gay et al. [2003]</td>
<td>USA (Minnesota)</td>
<td>NS</td>
<td>Dairy</td>
<td>NS</td>
<td>71.5 to 864 &amp; 84.9 to 675 µg m⁻² s⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Swine finishing</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Swine gestation</td>
<td></td>
</tr>
<tr>
<td>Patni et al. [1991]</td>
<td>Canada (Ontario)</td>
<td>Summer</td>
<td>Dairy</td>
<td>2.8 to 21.9% DM and 1.5 to 3.0 N as % DM</td>
<td>102 to 369 kg/site-dayᵇ</td>
</tr>
<tr>
<td>Zahn et al. [2001]</td>
<td>USA (Iowa)</td>
<td>NS</td>
<td>Swine</td>
<td>2.8 to 21.9% DM and 1.5 to 3.0 N as % DM</td>
<td>102 to 369 kg/site-dayᵇ</td>
</tr>
<tr>
<td>Amon et al. [2006]</td>
<td>Austria (Alps)</td>
<td>Summer</td>
<td>Dairy</td>
<td>Untreated slurry, uncovered</td>
<td>110.5 g m⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Untreated slurry, uncovered with wooden lid</td>
<td>60.0 g m⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Winter</td>
<td>Dairy</td>
<td>Untreated slurry, uncovered</td>
<td>72.5 g m⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Untreated slurry, uncovered with wooden lid</td>
<td>52.2 g m⁻³</td>
</tr>
</tbody>
</table>

ᵃ NS stands for not specified
ᵇ Emission rate measurements were respectively 102, 142, 233 et 369 kg/site-day for a deep pit, under a slatted floor, a circular concrete tank and 2 lagoons
ᶜ %DM stands for percentage of dry matter

Reading off table 2.5, for dairy slurry in concrete storages, ammonia emissions ranged from 21.1 to 864 µg m⁻² s⁻¹ while for swine they ranged from 30.0 to 675 µg m⁻² s⁻¹. This stresses the importance for Canada to measure ammonia emission rates from local large-scale facilities over long time spans to derive representative emission factors. Ammonia emission rates from exterior manure storages have also been shown to differ greatly from one season to another [Amon et al., 2007]. Atmospheric temperatures in Canada can fluctuate from -35 to +35 °C over a year, indicating again the importance of seasonal measurements.

The breakdown of the measurements taken in the Gay et al. [2003] study is presented in table 2.6.
Table 2.6: AMMONIA EMISSION RATES FROM CONCRETE STORAGE TANKS [Gay et al., 2003]

<table>
<thead>
<tr>
<th>Species</th>
<th>Type of animal</th>
<th>Number of observations</th>
<th>Number of farms</th>
<th>NH₃ emissions μg·m⁻²·s⁻¹ mean</th>
<th>standard deviation</th>
<th>minimum</th>
<th>maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>bovine</td>
<td>dairy</td>
<td>7</td>
<td>1</td>
<td>379</td>
<td>73.8</td>
<td>71.5</td>
<td>864</td>
</tr>
<tr>
<td>swine</td>
<td>finishing</td>
<td>4</td>
<td>1</td>
<td>402</td>
<td>298</td>
<td>84.9</td>
<td>675</td>
</tr>
<tr>
<td>swine</td>
<td>gestation</td>
<td>4</td>
<td>2</td>
<td>106</td>
<td>30.0</td>
<td>84.9</td>
<td>127</td>
</tr>
</tbody>
</table>

Chapter bibliography


CHAPTER 3
FOREMATTER ON SUBMITTED ARTICLES

Following the subject matter discussed in the previous sections, two scientific articles will follow suit in the following chapters:

- *Ammonia Emission Rates from Covered Concrete Manure Tanks in Eastern Canada*, presented in chapter 4, accepted by Transactions of the American Society of Agricultural and Biosystems Engineers (ASABE);

- *Ammonia Emission Rates from Dairy Livestock Buildings in Eastern Canada*, presented in chapter 5, submitted to The Institution of Agricultural Engineers (IAgrE) official publication, Biosystems Engineering.

The authors were presented as follows to both journals:

- Claudia V. Bluteau, main author (claudia.bluteau@mail.mcgill.ca);

- Daniel I. Massé, corresponding author and co-author (massed@agr.gc.ca);

- Roland Leduc, co-author, (roland.leduc@usherbrooke.ca).

Daniel I. Massé is a researcher with Agriculture and Agri-food Canada, Dairy and Swine Research and Development Center (2000 College Street, P.O. Box 90, Sherbrooke, Canada, J1M 1Z3). Roland Leduc is a professor in the department of Civil Engineering of Université de Sherbrooke (2500 Université Boulevard, Sherbrooke, Canada J1K 2R1). Claudia V. Bluteau is a graduate student that was affiliated with both the latter.

The main objective in both articles was to measure ammonia emission rates for at least two seasons from commercial large-scale infrastructures. Several other parameters were measured as a basis for comparison to other studies available in the literature. Methodologies used for ammonia emission rate measurements are detailed in each article. The validation of the equipment developed to do so is also explained in the articles.
CHAPTER 4

AMMONIA EMISSION RATES FROM COVERED CONCRETE MANURE TANKS IN EASTERN CANADA

4.1 Abstract

Manure storage is a well known source of anthropogenic ammonia emissions and has been the subject of numerous studies in Western Europe and in the United States of America. However, climate and manure management practices differ widely in Canada. Commercial dairy and swine manure storages covered by floating geomembranes were monitored for periods exceeding six months in Canada. The swine manure storage emitted negligible amounts of ammonia, from $5.9 \cdot 10^{-3}$ to $0.14 \ \mu g \cdot m^{-2} \cdot s^{-1}$ over the summer time, which is less than emission rates found in the literature for swine manure ranging between 45 and $875 \ \mu g \cdot m^{-2} \cdot s^{-1}$. The most substantial ammonia emissions at the swine facility occurred during manure mixing operations. A structural difference in the covering technology at the dairy manure storage rendered it less airtight than at the swine manure storage. The dairy manure storage emitted more substantial amounts of ammonia when unfrozen, 93 to $166 \ \mu g \cdot m^{-2} \cdot s^{-1}$, then when frozen during winter, 1.9 to $16 \ \mu g \cdot m^{-2} \cdot s^{-1}$. These emission rates are lower in magnitude than values found in the literature for dairy manure which ranged between 10 and $864 \ \mu g \cdot m^{-2} \cdot s^{-1}$.

4.2 Key words

Ammonia, Agriculture, Emission rates, Geomembrane, Manure storage

4.3 Introduction

There is an increased concern about losses in biodiversity that can potentially occur due to atmospheric ammonia deposition on sensitive ecosystems [Fraser et al., 2007]. Over-fertilization of ecosystems by ammonia deposition has been shown to cause terrestrial eutrophication and acidification of waterbodies and soils [Havlikova et al., 2008]. Furthermore, ammonia emissions from intensive livestock operations located in the vicinity of major cities induce favourable conditions for smog formation. Ammonia can react with nitrates and sulfates to produce ammonium nitrate and ammonium sulfate, these molecules being responsible for the formation of fine particulate matter and in turn smog [Cadle, 1972].
Manure handling, storage and spreading on cropland are responsible for 74% of anthropogenic atmospheric ammonia emissions in the world [Aneja et al., 2001]. Livestock production is deemed in Europe to be the most important source of ammonia in the atmosphere [ECETOC, 1994]. In Canada, data pertaining to ammonia emission rates from agricultural activities is very limited to date. Using reported data from Europe, Kurvits et al. [1998] estimated that livestock production was responsible for 82% of Canada's national ammonia inventory. However, climate as well as typical livestock management practices differ greatly between Canada and Europe.

4.4 Literature review

Ammonia emissions from manure are prone to high spatial and temporal variability due to the large number of factors involved in its volatilization, which affects the development of appropriate emission factors [Aneja et al., 2007]. For instance, livestock manure management practices such as the type of litter used [Amon et al., 2001; Rotz, 2004], the type of manure storage structure [Gay et al., 2003], and ambient conditions surrounding the manure storage [Ni, 1999] have been shown to affect several manure characteristics involved in the ammonia volatilization process. The rate of ammonia desorption from manure is highly dependent on the ionic strength, the ammonia concentration, pH and the temperature of manure [Arogo et al., 2003; Hafner et al., 2006; Ni, 1999]. Environmental conditions such as the velocity and temperature of the air-stream blowing over the manure surface can also affect ammonia volatilization rates [Arogo et al., 1999; Ni, 1999].

Geographically, the nearest extensive study to Eastern Canada on manure storage ammonia emission rates found in the literature was in the state of Minnesota in the United States of America [Gay et al., 2003]. However, the measurements were taken over such different temporal and spatial scales that they are inapplicable for deriving Canadian emission factors. Furthermore, ammonia emission rate measurements in Minnesota showed great variations. For dairy slurry in concrete storages, ammonia emissions ranged from 71.5 to 864 \( \mu g \cdot m^{-2} \cdot s^{-1} \) while for swine they ranged from 84.9 to 675 \( \mu g \cdot m^{-2} \cdot s^{-1} \).

Ammonia emission rates from exterior manure storages have also been shown to differ greatly from season to season [Amon et al., 2007]. Atmospheric temperatures in the location where this study took place in Canada can fluctuate from -35 to +35 °C over a year, indicating the importance of seasonal measurements.

Certain technologies have been developed to reduce ammonia losses from manure storages by limiting the surface exposed to ambient air. Floating covers made out
of natural or man-made materials (plastic, straw, oil) have been shown to reduce ammonia losses from 80 to 95% [Rotz, 2004; Xue et al., 1999]. Permanent lids can nearly eliminate ammonia storage losses when a appropriate seal is provided [Sommer et al., 1993]. Amon et al. [2006] showed for exterior pilot-scale concrete dairy manure storages in the Austrian Alps that a wooden lid reduced ammonia emission rates by 28% and 45% respectively during winter and summer conditions. Converting reported data from the Amon et al. [2006] study, ammonia emissions from the tanks ranged from 10 to 19 µg·m⁻²·s⁻¹. Approximately 10 metric tons of manure was stored in each storage for periods of 100 to 140 days. Of the available studies on atmospheric ammonia emissions from agriculture in Western Europe, the Austrian Alps climate is the most similar to Canada’s climate.

Given the lack of large-scale studies on manure management systems in Canada, and the novelty of covering manure storage structures with geomembranes, the scope of this study was to quantify ammonia emission rates from such systems. Two commercial manure storages were covered by geomembranes in Compton and St-François-Xavier-de-Brompton; both municipalities located in the Eastern Townships of Quebec in Canada. The storage in Compton contained dairy manure while the one in St-François-Xavier-de-Brompton contained swine manure.

4.5 Materials and methods

4.5.1 Manure management description

At the dairy farm, manure was transported daily from behind the stalls to a transfer tank by a chain conveyor. The bedding material used in the stalls was wood shavings and saw dust. Milk-house wastewater was flushed to the transfer tank to liquefy the manure so that it could be pumped daily to the exterior concrete storage tank. At the swine farm, pig slurry was flushed from several operations (farrowing, maternity, nursery) every other day towards the concrete storage tank with no addition of wastewater or bedding material.

4.5.2 Manure storage cover design

Both tanks were covered by a floating composite membrane durable enough to safely support foot traffic and snow load (Geomembrane Technologies Inc., Fredericton, Canada). Anchored to the perimeter of the circular concrete storage by stainless steel bands, a seal is provided by a gasket between the band and the perimeter. As illustrated in the photograph (figure 4.1, the cover is maintained at the surface of the manure by a series of weights positioned to accommodate manure level fluctuations.
and to accumulate rainfall for periodic pumping. This allows for gases produced within the storage to be drawn naturally towards an exhaust chimney.

![Figure 4.1: Photograph of the manure storage tank at the dairy farm](image)

As illustrated in figure 4.1 and 4.2, a completely sealed hatch skirt allowed access for a mixing pump used for removal operations. At the swine facility the vertical space allowing access to the pump was 61 cm, represented as H in figure 4.2. To provide flexibility in mixing operations at the dairy facility for several manure levels, the vertical space H was 152 cm.

![Figure 4.2: Profile view of manure access hatch on covered manure storages](image)

Sampling ports were installed in a concentric circle, as shown in figure 4.3. Sampling ports consisted of threaded PVC piping with screw-on tops, which were fixed to
the cover surface with a bolted flange. The diameter of the tanks was 29.0 m for the swine facility and 26.2 m for the dairy facility. Both tanks were 3.66 m high. Manure was sampled periodically at a maximum depth of 5 cm from the surface through these ports. On-site measurements of pH and temperature were done simultaneously with a portable with an ISFET probe (IQ150, IQ Scientific, USA). Total and volatile solid fractions (%TS and %VS) were measured following APHA [1992] standards while total Kjeldhal nitrogen (TKN) and total ammonia as nitrogen ([NH₄⁺ – N]) concentrations were measured using an automated titration method (Kjeltech 2460, Foss, Sweden). Each sample was measured in duplicate.

![Diagram of manure tanks with sampling ports and hatch access](image_url)

**Figure 4.3:** Location of manure sampling ports, thermocouple (port T) and hatch access from a topview of the manure tanks

An 8-point vertical temperature profile of the manure was measured continuously in both storages using thermocouples (Type T, Omega, USA). Its location relative to manure sampling ports and the hatch access is indicated as T in figure 4.3. The manure level in the tanks was also measured periodically, by surveying the surface relative to a designated benchmark or directly through the hatch access doors.

### 4.5.3 Manure gas production monitoring

A programmable logic-controller (Momentum M1, Modicon, Schneider Automation Inc., USA) was used to record air temperature, pressure and flowrate. The system was designed and programmed by ADI Limited (Fredericton, Canada).

The covered manure storages were vented to the atmosphere by an exhaust chimney connected to an industrial helicoidal blower (Sutorbilt 2MP, Gardner Denver, USA).
The blower would start once the measured gauge pressure under the cover attained 60 Pa (Rosemount 3051, Emerson Process Management, Rosemount Division, Chanhassen, MN, USA), and would stop once the pressure would reduce to 25 Pa. Gas exhaust rates were measured by counting the number of blower revolutions with an inductive proximity switch (Omron E2E, Japan), one revolution displacing a constant volume of 0.48 dm³ of gas. The maximum exhaust rate that could be provided by the blower was 2549 L·min⁻¹ (90 cfm). The blower calibration was verified by taking cross-sectional measurements of pressure velocities in the inlet pipe with a pitot tube (ADM-770C Airdata Multimeter, Shortridge Instruments Inc., USA). Biogaz flowrate measurements using the number of blower revolutions were exactly the same as those obtained with the pitot-tube, and such within their respective resolutions. Gas flowrates were corrected for air density variations by continuously measuring temperature of the exhaust gas (TT205 Thermocouple transmitter type T, Mod-tronic Instruments Limited, Canada) and atmospheric pressure (Davis Instruments Weather Monitor, Hayward, USA).

4.5.4 Gas flow and ammonia concentration determination

Swine facility

Acid traps, depicted in figure 4.4 were used for ammonia measurements at the swine facility. Gas samples were drawn by a rotary vane vacuum pump from the exhaust chimney to the acid traps for periods lasting 24, 48, 72, 144 or 216 hours (3032 Series, Gast Manufacturing Inc., USA). Both traps contained 450 mL of 0.5 N sulfuric acid. Remaining acid volumes were measured after each sampling period to account for evaporation losses. Sample ammonium concentrations were measured by an automated titration analyzer (Kjeltech 2460, Foss, Sweden). In three initial field trials and 19 laboratory trials with standard gas (1.8% ammonia), the mass of ammonium in the second trap was always less than 1.5% of the mass in the first trap. The second trap was then eliminated to reduce handling in the field. A natural gas counter was used as volumetric flowmeter to measure biogas sampling rates (Gallus 2000 Actaris, Luxembourg). Continuous ambient temperature and pressure measurements from the weather station were sufficient to account for gas density fluctuations. The acid traps were placed before the flowmeter as depicted in figure 4.4 and acted as a heat sink for the biogas samples because temperature would increase significantly when passing through the rotary vane pump. The specific gravity of the sampled gas was determined by establishing its composition from chromatograph analysis of triplicate gas samples taken directly from the chimney with the 10-cc syringes. This was done for each observation period. This was necessary for proper conversions from volumetric natural gas measurements to ammonia mass flow rates.
Dairy facility

At the dairy facility, a vacuum pump continuously drew gas samples from the blower inlet and conveyed them toward an infrared MGA-3000 analyzer (ADC Gas Analysis ltd, UK) through heated Teflon® tubing for periods ranging from three to eleven days. The analyzer was installed in an insulated heated box which maintained the ambient temperature at 25°C. The analyzer measured with a precision of 1% fullscale the concentrations of methane, ammonia, carbon dioxide and oxygen, over respective scales of 0-100%, 0-2.00%, 0-100% and 0-25.0% respectively. Proper calibration of the analyzer was verified with standard gases (1.8% ammonia in air and 100% methane) prior to every sampling period (Praxair, Canada). Triplicate gas samples were taken on nine occasions between January 22 and April 24 2007 in 10-cc syringes through a septum tap to counter-verify methane and carbon dioxide measurements given by the infrared analyzer. Gas samples were injected the same day at the laboratory into a gas chromatograph, model HachCarle 400 AGC (Hach, Loveland, CO, USA). The chromatograph was configured following 131-C application (stack analysis), with a set temperature of 80°C, and nitrogen was used as the support gas. The chromatograph established the composition of the samples relative to nitrogen, methane, carbon dioxide and hydrogen sulfide gas.
4.6 Results and discussion

Average gas exhaust rates from the manure tanks during each of the observation periods ranged between 38 and 218 L \cdot min^{-1} at the swine facility, and 86 to 566 L \cdot min^{-1} at the dairy facility. Gas volumes were all normalized to a temperature of 0°C and a pressure of 1 bar. Instantaneous gas exhaust rates reached the maximum blower capacity of 1954 L \cdot min^{-1} (69 cfm) at the dairy facility.

4.6.1 Swine manure storage

The manure surface under the insulated cover remained unfrozen year-round at the swine facility. Measured physico-chemical parameters of the manure surface are given in table 4.1. Total ammonia as nitrogen, total Kjeldhal nitrogen and pH levels remained fairly constant through time and similar across the seven available sampling ports. The %VS and %TS measurements ranged from 0.15% to 0.92% and 0.41% to 1.42% respectively, which explains the high coefficient of variations associated with these low levels of solids measured in the swine manure.

Table 4.1: MEASURED PHYSICO-CHEMICAL PARAMETERS OF MANURE SURFACE AT THE SWINE FACILITY

<table>
<thead>
<tr>
<th>Parameter</th>
<th>N*</th>
<th>Mean</th>
<th>Coefficient of variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>VS(%)</td>
<td>49</td>
<td>0.38</td>
<td>0.74</td>
</tr>
<tr>
<td>TS(%)</td>
<td>49</td>
<td>0.68</td>
<td>0.52</td>
</tr>
<tr>
<td>TKN (mg \cdot L^{-1})</td>
<td>47</td>
<td>1493</td>
<td>0.12</td>
</tr>
<tr>
<td>$</td>
<td>N - NH_4^+</td>
<td>(mg \cdot L^{-1})$</td>
<td>47</td>
</tr>
<tr>
<td>pH</td>
<td>47</td>
<td>7.5</td>
<td>0.02</td>
</tr>
</tbody>
</table>

* N=Number of observations

Ammonia emission measurements that are presented in table 4.2 were made between May and November 2007 from the covered swine manure storage and ranged from $5.9 \cdot 10^{-3}$ to $0.14 \ \mu g \cdot m^{-2} \cdot s^{-1}$. In comparison, ammonia emission rates from uncovered swine manure tanks in Minnesota ranged between 85 and 675 $\mu g \cdot m^{-2} \cdot s^{-1}$ [Gay et al., 2003], more than those measured from the swine manure storage in this study.

Furthermore, a pilot-scale swine manure storage in Austria covered with a wooden lid emitted 45 $\mu g \cdot m^{-2} \cdot s^{-1}$ of ammonia when converting reported data [Amon et al., 2007]. This is substantially more than the swine manure storage in this study which emitted between $5.9 \cdot 10^{-3}$ and $0.14 \ \mu g \cdot m^{-2} \cdot s^{-1}$ of ammonia. In the Austria study, ammonia emission rates were measured on numerous occasions over an experimental period of 200 days, and average manure temperature was 17°C. In this study, the
Table 4.2: AMMONIA (NH\textsubscript{3}) EMISSION RATES FROM COVERED CONCRETE DAIRY AND SWINE MANURE

<table>
<thead>
<tr>
<th>Livestock Type and Manure Condition</th>
<th>N*</th>
<th>Ammonia emission rates in ( \mu g \cdot m^{-2} \cdot s^{-1} )</th>
<th>Mean</th>
<th>Coefficient of variation</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dairy, unfrozen manure</td>
<td>13</td>
<td>140</td>
<td>0.16</td>
<td></td>
<td>93-166</td>
</tr>
<tr>
<td>Dairy, frozen manure</td>
<td>16</td>
<td>6.5</td>
<td>0.76</td>
<td></td>
<td>1.9-16</td>
</tr>
<tr>
<td>Swine, unfrozen manure</td>
<td>8</td>
<td>0.071</td>
<td>0.71</td>
<td></td>
<td>0.0059-0.14</td>
</tr>
</tbody>
</table>

* N=number of observations

average manure temperature throughout the vertical profile at the swine facility was 16 °C when considering periods where ammonia emission measurements were taken. The manure profile measurements of the swine facility for each observation period are given in table 4.3.

Table 4.3: VERTICAL PROFILE OF MANURE TEMPERATURE AT THE SWINE FACILITY IN DEGREES CELSIUS

<table>
<thead>
<tr>
<th>Date</th>
<th>Mean</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>May 7 to 16 2007</td>
<td>9.4</td>
<td>0.12-26</td>
</tr>
<tr>
<td>June 5 to 7 2007</td>
<td>15</td>
<td>4.9-25</td>
</tr>
<tr>
<td>Sept. 18 to 20 2007</td>
<td>18</td>
<td>3.1-32</td>
</tr>
<tr>
<td>Oct. 1 to 3 2007</td>
<td>22</td>
<td>8.9-34</td>
</tr>
<tr>
<td>Nov. 5 to 8 2007</td>
<td>9.8</td>
<td>1.1-11</td>
</tr>
</tbody>
</table>

As shown in figure 4.5, the highest ammonia emission rates of 0.14 and 0.13 \( \mu g \cdot m^{-2} \cdot s^{-1} \) occurred respectively for the May 7 to 16 and September 18 to 20 2007 periods when removal operations were taking place. On these occasions, manure is continuously agitated by a tractor driven mixing pump. Ammonia emission rates were respectively 0.13, 0.11 and 8.9 \( \cdot 10^{-2} \mu g \cdot m^{-2} \cdot s^{-1} \) for the observation periods of September 18 to 20, October 1 to 3 and October 18 to 19, of the year 2007. At these times manure levels were below the 61-cm vertical opening at the bottom of the hatch skirt and the blower was running continuously.

As manure levels rose between September 18 and October 19 2007, ammonia emission rates dropped. All other ammonia emission rate observations were done at times where manure was undisturbed except for irregular inputs of fresh manure at an average rate of 18 m\textsuperscript{3} \cdot day\textsuperscript{-1}. The lowest ammonia emission rate of 5.9 \( \cdot 10^{-3} \mu g \cdot m^{-2} \cdot s^{-1} \)}
Figure 4.5: Manure temperature, manure height and ammonia emission rates at the swine facility measured on November 8 to 14 2007, occurred when mean ambient temperature was at its lowest, -1.1°C.

4.6.2 Dairy manure storage

At the dairy facility, a sludge-like crust had formed at the manure surface from August to December 2006 continuously. The manure surface was frozen between January 23 and March 3 2007 continuously. The blower was able to draw fresh air underneath the cover since the hatch doors were not airtight. Average daily methane composition measured by the MGA-3000 did not exceed 11% and manure levels were often below the 152-cm vertical opening at the bottom of the hatch skirt.

Vertical profile of manure temperatures measured simultaneously with ammonia emission rates are given in table 4.4. Average manure temperature was 27°C in August 2006 and 4.9 °C in December 2006. The manure surface remained unfrozen during both of these months.
Table 4.4: VERTICAL PROFILE OF MANURE TEMPERATURE AT THE DAIRY FACILITY IN DEGREES CELSIUS

<table>
<thead>
<tr>
<th>Date</th>
<th>Manure condition</th>
<th>Mean</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>August 2006</td>
<td>Unfrozen</td>
<td>27</td>
<td>23-33</td>
</tr>
<tr>
<td>December 2006</td>
<td>Unfrozen</td>
<td>4.9</td>
<td>0.3-9.5</td>
</tr>
<tr>
<td>January 2007</td>
<td>Frozen</td>
<td>1.8</td>
<td>0.010-5.0</td>
</tr>
<tr>
<td>February 2007</td>
<td>Frozen</td>
<td>1.5</td>
<td>0.01-3.4</td>
</tr>
<tr>
<td>March 2007</td>
<td>Frozen</td>
<td>2.0</td>
<td>0.12-6.7</td>
</tr>
</tbody>
</table>

[1] Frozen surface measurements were excluded

From the average ammonia emission rates given in table 4.2, the dairy facility emitted 21 times more ammonia in its unfrozen than in its frozen state. Indeed, by observing figure 4.6, a sudden drop in emissions occurred between December 31 2006 and January 23 2007. Ammonia emission rates measured at the dairy facility varied from 1.9 to 170 μg·m⁻²·s⁻¹; which fall on the lower side of the range measured by Amon et al. [2006] in Austria and Gay et al. [2003] in Minnesota for dairy manure stored in concrete tanks: 10 to 864 μg·m⁻²·s⁻¹.

Figure 4.6: Manure temperature, manure height and ammonia emission rates at the dairy facility
The highest ammonia emission rate when manure was frozen was 16 \( \mu g \cdot m^{-2} \cdot s^{-1} \) and occurred both on January 23 and February 27 2007. The blower was non-operational from January 1 to 22 nor from February 15 to 27 2007 because of ice formation around the blower. These high emission rates probably represent accumulated gaseous ammonia underneath the cover.

Unlike the swine manure surface, ammonia as nitrogen concentrations varied considerably across the four available sampling ports at the dairy facility as can be observed in figure 4.7.

![Figure 4.7: Total ammonia as nitrogen concentrations of manure surface at the dairy facility in mg L\(^{-1}\)](image)

Figure 4.7: Total ammonia as nitrogen concentrations of manure surface at the dairy facility in mg L\(^{-1}\)

The highest ammonia as nitrogen concentrations in the surface manure were at Port C. The latter port was the closest to the underground manure pipe inlet where manure was pumped daily from the building at an average rate of 4.7 m\(^3\)· day\(^{-1}\). The lowest concentrations were always measured at port D, which was the closest to the exhaust chimney. This suggests that more ammonia was volatilized from the surface near the exhaust chimney. Furthermore, nitrogen as ammonia concentration in the manure surface at Port D was 1282 mg · L\(^{-1}\) once it thawed in April 2007, much greater than
prior to freezing in September or December where measurements were respectively 408 and 584 mg L⁻¹. This supports the data that show much less extensive ammonia volatilization when the manure surface is frozen than when unfrozen.

Manure TKN concentrations, %VS, %TS and pH were measured in manure samples from the four available ports on December 20 2006 and April 24 2007. The average, coefficient of variation, maximum and minimum values are provided in table 4.5.

Table 4.5: MEASURED PHYSICO-CHEMICAL PARAMETERS OF MANURE SURFACE AT THE DAIRY FACILITY

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mean</th>
<th>Coefficient of variation</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>VS(%)</td>
<td>15</td>
<td>0.38</td>
<td>6.7-28</td>
</tr>
<tr>
<td>TS(%)</td>
<td>17</td>
<td>0.38</td>
<td>8.0-32</td>
</tr>
<tr>
<td>TKN (mg L⁻¹)</td>
<td>5272</td>
<td>0.48</td>
<td>1801-10998</td>
</tr>
<tr>
<td>pH</td>
<td>7.0</td>
<td>0.07</td>
<td>6.5-8.0</td>
</tr>
</tbody>
</table>

4.7 Conclusion

The insulated floating cover nearly eliminated ammonia emissions from a concrete manure storage in Canada when a proper seal was maintained. Indeed, the swine manure storage emitted between 5.9 \times 10⁻³ to 0.14 \mu g m⁻² s⁻¹ of ammonia during summer conditions, less than emission rates found in the literature which ranged from 45 to 875 \mu g m⁻² s⁻¹ [Amon et al., 2007; Gay et al., 2003].

On the other hand, the dairy manure facility cover was much less airtight, resulting in greater ammonia emissions ranging between 1.9 and 166 \mu g m⁻² s⁻¹. These emission rates were lower in magnitude than values found in the literature which ranged between 10 and 864 \mu g m⁻² s⁻¹ [Amon et al., 2007; Gay et al., 2003]. The large range of emission rates measured at the dairy facility in this study was mainly associated with large fluctuations in manure temperatures over the experimental period which extended over three seasons; summer, autumn and winter. The manure surface froze over in the beginning of January 2007, causing ammonia emission rates to plummet from 151 \mu g m⁻² s⁻¹ to 16 \mu g m⁻² s⁻¹. Therefore, deriving specific ammonia emission factors for frozen and unfrozen manure surface is relevant for the Canadian context.

The equipment used to measure biogas production rates and ammonia concentrations were checked against standards or equipment used for similar purposes. Considering that only two farms located in neighbouring counties were the subject of this
study. Many more, including uncovered manure storages, must be studied to derive ammonia emission factors for Canadian agriculture. This is especially true considering the wide array of climates and management practices that can be found over the vast Canadian territory.

4.8 Acknowledgments

The authors wish to acknowledge the initiative and financial support of GAPS (Information Gaps in Water Quality and Nutrients) from Agriculture and Agrifood Canada. They would also like to mention the technical support of Robert Porter from ADI Limited (Fredericton, Canada) and Brennan Sisk from Geomembrane Technologies inc. (Fredericton, Canada). They would also like to thank the owners of both commercial farms, Mr. Jean-Noël Groleau and Mr. Roberto Rodriguez, for their precious collaboration.

Article bibliography


CHAPTER 5

AMMONIA EMISSION RATES FROM DAIRY LIVESTOCK BUILDINGS IN EASTERN CANADA

5.1 Abstract

Gaseous ammonia emissions from livestock production are deemed responsible for the acidification of several ecosystems and for the formation of PM$_{2.5}$. The latter induces adverse health effects in humans, mostly respiratory ailments. In this study, ammonia emission rates from two tie-stall commercial dairy buildings were monitored in Canada. Buildings studied were mechanically ventilated and livestock management practices were typical of Eastern Canada. Ammonia emission measurements done at building A during the months of February and March 2007 ranged from 3.77 to 6.80 g • day$^{-1}$ • animal$^{-1}$ while those performed at building B during summer 2007 ranged from 11.33 to 18.20 g • day$^{-1}$ • animal$^{-1}$. These values fall within the range of ammonia emission rates found in the literature for studies completed in Western Europe: 0.1625 g • day$^{-1}$ • AU$^{-1}$ to 23.38 g • day$^{-1}$ • animal$^{-1}$. An electrochemical ammonia analyser was used at building A for continuous measurements while a titration method using acid traps was used at building B to measure average ammonia concentrations. Propeller anemometers were developed to measure building ventilation flowrates. The precision of the equipment used to measure building ventilation rates and gaseous ammonia levels inside the building were also evaluated at both farms.

5.2 Key words

Ammonia, Agriculture, Gaseous Emissions, Dairy housing

5.3 Introduction

Atmospheric ammonia emissions are responsible for several adverse effects on natural habitats in Europe [Bobbink et al., 1998; Grennfelt et al., 1986]. Other than acidification effects in soils, soil water, groundwater and surface waters via dry deposition and wet precipitation [Erisman et al., 2007], ammonia emissions can react with nitrates and sulphates in the atmosphere to produce smog [Cadle, 1972]. Livestock production is deemed to be the greatest contributor of anthropogenic ammonia emissions in Europe and Canada [ECETOC, 1994; Kurvits et al., 1998]. However, very few field measurements have been done in Canada.

Several large-scale studies measuring ammonia emission rates from dairy livestock buildings have been conducted in Europe and in the United States of America [Gay et
Livestock animals typically use less than 30% of the nitrogen they ingest, which leaves 50 to 80% to be excreted in urine and 20 to 30% in feces. Urea is the source of 97% of all nitrogen contained in urine [McCrory et al., 2001]. Transformation of urea into ammonium ions is dictated by ureic activity, where urease enzymes contained in feces can readily decompose the urea in urine. Therefore, limiting contact between feces and urine should limit ammonia emission rates. Furthermore, ureic activity increases exponentially with increasing temperature. Ureic activity is also negligible at temperatures below 10°C [Rotz, 2004]. This can occur rapidly during short-term manure storage in dairy buildings, with a complete conversion of urea into ammonium within a few hours. The following environmental and manure physico-chemical parameters affect ammonia volatilization rates from livestock production infrastructures:

- Temperature and speed of air just over the manure surface [Kroodsma et al., 1993; Ni, 1999];

- Ionic charge, manure ammonia concentration, pH and manure temperature [Ni, 1999; Arogo et al., 2003; Hafner et al., 2006].

Furthermore, very few studies indicated the procedures used to evaluate the accuracy of building ventilation flowrate measurements or gaseous ammonia concentration measurements in livestock buildings. Yet, no standardized procedures exists for these matters in agricultural air quality studies [Aneja et al., 2007].

In this paper, ammonia emission rates from two dairy livestock buildings in Canada are presented. These values will serve as a starting point for a national ammonia inventory from agriculture, which has previously been using values from other countries. The systems developed to do so and the procedures used to evaluate their inherent precision are described to further increase knowledge in agricultural air quality methodologies.
5.4 Materials and methods

5.4.1 Building and dairy herd descriptions

Considering the difficulties inherent to air flow measurements through wall openings of naturally ventilated barns [Demmers et al., 2001], negative-pressure, mechanically-ventilated buildings were chosen for the study. Two tie-stall commercial dairy barns, typical of Eastern-Canada, were retained. Building A and B were located in Cookshire and in Compton, respectively, both municipalities being in the province of Quebec. Their respective animal housing surface areas were 371 and 1022 m². Between April 2006 and January 2007, lactating cows in building A and B each produced an average of 25.7 and 18.7 kg of milk per day respectively. In both buildings, manure was transported daily from behind the stalls to a transfer tank by chain conveyors. Wood shavings were used at both facilities while building A also used straw. Milk-house wastewater was also conveyed to the transfer tanks, so that manure slurry could be pumped daily to an exterior storage tank. Weekly recording of the number of animals present in both buildings were taken. The number of dairy animals in building A ranged from 67 to 75 animals in total, distributed as 23 to 41 replacement animals and 36 to 44 lactating cows. Dry cows were housed in an adjacent barn. For building B, the number of animals varied significantly throughout the experimental period, since part of the herd was sent outside during daytime hours in the summer season. The owners of building B also began housing equine and caprine animals subsequent to project commencement. The breakdown of the number of animals housed in both buildings over the measurement periods are given in Tables 5.3 and 5.6. Lactating cows at building A were typically fed a total mixed ration (TMR) of 7 kg dry crushed corn, 2 kg Shur-gain commercial mix (Nutreco Canada Inc., Canada) and 10.5 kg round hay bales. Lactating cows at building B were fed dry hay and a typical TMR of 42% alfalfa, 25% corn silage, 6% hay, 4% barley, 15% dry crushed corn, 3% soy and 5% micronutrients. The TMR fraction of feed was 93% of the total feedstuff served. Nutritional feed values of the ingredients contained in both diets are shown in table 5.1. Overall estimated percent protein of the feedstuff on a drymatter basis was 13% at building A and 14% at Building B for the milking cows. For building A, the non-milking cows were fed the same rations as the milking cows, only in smaller portions. For building B, the non-milking cows were fed a ration solely composed of variable proportions of corn and alfalfa silage mixed with mineral supplements.

At each farm, thermostatically controlled exhaust fans of two different diameters were present, the smaller ones used for winter ventilation and the larger ones for summer ventilation. The ventilation system of building A was composed of five 40.6-cm and three 122-cm diameter axial fans (Vic Ventilation, Canada), coupled to manually
Table 5.1: NUTRITIONAL BREAKDOWN OF DAIRY FEEDS

<table>
<thead>
<tr>
<th>Component</th>
<th>Building A</th>
<th>Building B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shur-gain</td>
<td>Corn</td>
</tr>
<tr>
<td>Dry matter, DM (%)</td>
<td>93.6</td>
<td>87.3</td>
</tr>
<tr>
<td>Protein (% of DM)</td>
<td>35.4</td>
<td>9.2</td>
</tr>
<tr>
<td>Fat (% of DM)</td>
<td>2.2</td>
<td>4.0</td>
</tr>
<tr>
<td>ADF (% of DM)</td>
<td>10.5</td>
<td>3.3</td>
</tr>
<tr>
<td>NDF (% of DM)</td>
<td>13.5</td>
<td>9.0</td>
</tr>
<tr>
<td>Lignin (% of DM)</td>
<td>-</td>
<td>0.18</td>
</tr>
<tr>
<td>Starch (% of DM)</td>
<td>-</td>
<td>68.9</td>
</tr>
<tr>
<td>Sugars (% of DM)</td>
<td>-</td>
<td>3.6</td>
</tr>
</tbody>
</table>

* Typical TMR composed of 42% alfalfa, 25% corn silage, 6% hay, 4% barley, 15% dry crushed corn, 3% soymeal and 5.0% micronutrients

controlled inlets. The 40.6-cm fans being between 20 and 30 years old made inapplicable the use of current manufacturing curves. The ventilation system of building B was composed of four 122-cm and four 50.8-cm diameter axial fans (models 3105400 and EF 4116000, Ventec, Canada) coupled to electronically controlled inlet openings. The ventilators at building B were less than 10 years old. Fans at both buildings were set to rotate at maximum speed, except for three 40.6-cm diameter fans at building A that could run at two different power settings. The 40.6 and 50.8-cm diameter fans were protected by weather hoods.

A mass balance approach derived from Kinsman et al. [1995] was used in this study. The difference between the mass of ammonia entering and leaving the building represents the ammonia volatilized from the building. Assuming no mass accumulation of air in the building under negative pressure, the air flow rate exhausted by the fans is equivalent to the air flow rate entering through all wall openings. By measuring the ammonia content of the air at each fan outlet and two distinct inlets in conjunction with the ventilation rate of each fan, a mass balance could be performed. The location of sampled air inlets and fans for both buildings are shown in figures 5.1 and 5.2.

5.4.2 Building ventilation measurements

Propeller anemometers of identical diameter to the fans present in each building were used to measure fan ventilation flow rates. Each anemometer was calibrated in a chamber-style wind tunnel conforming to ANSI/ASHRAE 51-1999 [2000] standards by installing them in-line with its corresponding fan. Different vacuum conditions in the chamber were produced by varying the power output of the service fan. The rotational velocities, as indicated by proximity sensors installed on the anemometers...
1.2.3.4, 5: Exhaust Air Sampling Locations (winter ventilation)
6.7.8: Exhaust Air Sampling Locations (summer ventilation)
9, 10: Inlet Air Sampling Locations

Figure 5.1: Location of inlet and outlet air samples at building A

1.2.3.4: Exhaust Air Sampling Locations (summer ventilation)
5, 6, 7, 8: Exhaust Air Sampling Locations (winter ventilation)
9, 10: Inlet Air Sampling Locations

Figure 5.2: Location of inlet and outlet air samples at building B
(Omron E2E, Japan), were linearly correlated to normalized air flow rates measured
by the array of pitot tubes. The coefficient of determination of the linear correlations
exceeded 0.990 in all cases. All 40.6-cm diameter anemometers were calibrated at
both available speed settings.

At building A, the calibrated anemometers were installed in the same position as
during wind tunnel trials for the whole course of the measurement period. Anemome-
ter rotational speeds correlated to normalized air flow rates. At building B, the
anemometers were used to calibrate each axial fan by correlating air flow rates given
by the rotational speed of the anemometers to pressure differential readings between
the inlet and outlets of each fan (Modus T40, General Electric, USA). Ambient temper-
ature and pressure measurements were required to correct for air density differences
between on-site fan calibration procedures and those occurring during wind-tunnel
testing (Thermocouple Type T; Weather Monitor II, Davis Instruments, USA). Once the
calibration was completed, the anemometer was removed and second order correlation
curves between pressure differentials and normalized air flow rates were generated.
Airflow density differences between on-site fan calibration procedures and on-site ex-
perimental measurements were not accounted for. For the 122-cm diameter fans,
the air flow rate increase when removing the anemometer was evaluated to be 7.4%
from sequential wind tunnel testing of the fan with and without the anemometer. No
significant difference was noted for the small diameter fans. Magnetic proximity sen-
sors (SRF-3A, Microswitch, Honeywell USA) coupled with magnets placed on the fans,
indicated when the fans were actually running during the measurement period.

At building B, two differential pressure sensors were located in close proximity to the
inlet air sampling locations (locations 9 and 10) at the far end of the building, away
from the exhaust fans. Mounted on opposite walls facing each other, the sensors
measured pressure differentials between indoors and outdoors across the wall.

Ventilation data were discarded when one of the differential pressure sensors indi-
cated a positive pressure inside the building. This often occurred during high wind
episodes across the building, which were measured by the weather monitor. Indeed,
a suction would happen on the exterior downwind wall which could cause contami-
nated air to escape from the side of the building instead of through the fans. During
these wind episodes, the pressure was sometimes equal on both sides of the down-
wind wall, but the windward pressure transducer indicated a vacuum exceeding 5 Pa
on the interior wall. On these occasions, the ventilation data were also discarded since
the vacuum on the interior windward wall was not induced by the fans, but by wind
pressure on the external wall.
Ventilation data was also discarded when not all of the 122-cm diameter fans were in function. Indeed, exhausted air through one of the fans was observed to flow back into the building through the fans not in function. These inputs of ammonia and methane could not be accounted for in the building mass balance.

5.4.3 Air sampling, ammonia and methane measurement systems

A data acquisition and control system (Fieldpoint, National Instruments, USA) recorded all signals in each building. The program was developed in a LABVIEW™ environment (National Instruments, USA). The computer communicated with all peripheral devices via RS232 series communication ports. The data acquisition system controlled the sequential sampling of air from one location to the next, while building ventilation rates were measured continuously.

Both farms were equipped with an electronically controlled air sampling system that continuously conveyed samples to an electrochemical ammonia analyzer, which recorded readings on a scale of 0 to 50 ppm (TX guard-IS+, Crowcon, United Kingdom). Standard gas (47.9 ppm NH₃ in nitrogen, Praxair, Canada) was used in the laboratory to verify proper functioning of the apparatus before field installation. The precision of the analyzer being 1% of its full scale, accurate ammonia mass balances during summer was not possible at building B because the difference in ammonia concentration between each outlet and the average at the inlets was less than 1 ppm 93% of the time. Indeed, average ventilation rates exceeded 60000 m³·h⁻¹ at building B, corresponding to 17 building air changes per hour. An alternate system using acid traps was used in this case. For building A, the difference between ammonia concentrations at the outlets and the inlets ranged between 1 and 13 ppm 83% of the time. The average difference was 3.1 ppm with a standard deviation of 1.15 ppm. Ventilation flow rates at building A did not exceed 11000 m³·h⁻¹ during the experimental period. This is equivalent to 6 building air changes per hour. The use of the electrochemical ammonia analyzer at building A was considered acceptable over these periods.

At dairy housing A, air was sampled sequentially from every fan and from two different air inlets every 14 minutes. A Teflon® tubing connected each sampling location to the air conditioning system. Each air sample flowed to its corresponding two-way solenoid valve (Model 6011, Bürkert, Germany) mounted on the main manifold. A vacuum pump (3032 Series, Gast Manufacturing Inc., USA) constantly created a vacuum in order to draw air from the manifold. Each valve sequentially opened for periods ranging from 30 seconds to 2 minutes, allowing one sample to flow through a 50-µm dust filter (Festo VAF Vacuum filter, India). These sampling times were based on the air volume that could be contained inside the tubing and the sampling flowrate in order to
ensure complete flushing of the lines prior to each sampling. The sample air flow then
split by the ammonia analyzer and an infrared methane analyzer (MGA3000,
ADC Gas Analysis Ltd, United Kingdom) preceded by a thermoelectric dryer (Universal
Analyzers 620SS, USA) and a 1-μg Teflon® dust filter.

At dairy housing B, ammonia concentrations were monitored weekly for 24-hour
periods from one 122-cm diameter fan (location 1 on figure 5.2). Due to relatively
long sampling periods and the use of Teflon® tubing, ammonia losses by adsorption
were assumed to be negligible. The air sampling system was placed in close prox-
imity to fan 1. The system made use of two diaphragm vacuum pumps installed in
parallel (15D series, Gast Manufacturing Inc., USA), conveying air through two acid
traps in series at flow rates ranging from 9 to 12 L min⁻¹. Flowrates were measured
with a 20 L min⁻¹ electronic mass flow meter (FMA-1600A, Omega, USA), having a
precision of 1% of its full scale. Both trap containers were made of clear PVC plastic
and initially contained 450 mL of 0.5 N sulphuric acid. Remaining acid volumes after
sampling was measured to take in account evaporation losses. The aqueous ammo-
nia content in both traps was determined using an automated titration method in the
laboratory (Kjeltech 2460, Foss, Sweden). The latter, in conjunction with the traps air
sampling rate measurements, were used to derive the ammonia concentration in the
air exhausted by fan 1. The gaseous ammonia concentration at fan 1 was assumed
equivalent for all rotating fans since they were all located in close proximity to one
another. Indeed, only the four 122-cm diameter fans and the 50.8-cm diameter fan
(locations 1 to 5 in figure 5.2) were in function during field measurements. Ammonia
emission rates from the building was extrapolated from one fan to the total building
using the sum of airflow measurements at all rotating fans.

5.4.4 Precision evaluation of acid traps

The use of acid traps for field measurements was validated in the laboratory. Five
experimental trials were performed where standard gas containing 1.80% ammonia
in air (Praxair, Canada) was conveyed through Teflon® tubing for 60 minutes from
the cylinder toward the experimental set-up at a controlled rate. Such a high concen-
tration was used in order to achieve detectable ammonia levels in both acid traps
rapidly over several consecutive trials subsequent to a relatively short flushing in
phase. The resolution of the titration equipment was limiting for precise measure-
ment of the low ammonia contents expected in the second acid trap. Both acid traps
contained 450 mL of 0.5 N sulphuric acid. An electronic mass flow meter with a full
scale of 0 to 2 L min⁻¹ (FMA-1600A, Omega, USA) was used to maintain the flow
rate at 2.00 L min⁻¹, standardised at 25°C and 101.32 kPa, for each trial. The pre-
cision of the flowmeter was 1% of its full scale. Acid was used to rince the traps once

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sampling acid was removed. Between each trial, each trap was emptied one at a time and the mass flow meter valve was shut in order to limit contact between ambient air and the interior of the tubing connecting the set-up to the cylinder. This was done to limit ammonia desorption losses from the apparatus. Ammonia content of the rinse acid and the acid contained in both traps was measured similarly to field samples using the automated titration apparatus (Kjeltech 2460, Foss, Sweden). Ammonia concentration of the standard gas was then derived and compared as a percentage to its certified by the manufacturer value of 1.80%.

5.4.5 Precision evaluation of ventilation measurements

The precision of the ventilation measurement system as a whole was determined prior to ammonia emission measurements at each building. Known quantities of methane was injected within the building for twenty minutes while the animals were inside, at a rate equivalent to two to four times the herd's average methane production rate. To do so, a cylinder of grade 2 pure methane (Praxair, Canada) was mounted on a 75-kg capacity digital scale (GSE scale systems GSE 465, Novi, USA) that communicated via RS232 series communication port with the computer. The resolution of the 75-kg capacity scale was 1 gram. The change in mass of the cylinder was recorded every minute during methane release trials. Methane gas flow from the cylinder toward an extensive network of perforated vinyl tubing throughout the building was controlled by a solenoid valve (Model 8320G184, Asco Valve, Canada).

Methane release trials were accomplished between midnight and 4 am since herd methane production was most stable at those hours, as cows were fed several hours beforehand. Furthermore, building B was not subject to high eastern winds at those times, which would have rendered methane emission measurements invalid due to insufficient vacuum within the building. The data acquisition system recorded methane emissions from the building for two hours following methane injections. By subtracting the baseline herd production curve to the total building methane emission curve, the quantity of injected methane from the cylinder recovered by the measurement system could be obtained by numerical integration. The latter was compared to the quantity of released methane given by the scale measurements in order to obtain a percentage of recovered methane.

5.5 Results and discussion

5.5.1 Precision of ventilation measurements

At building A, 14 methane injection trials were done for winter ventilation between December 14, 2005 and January 22, 2007 and six were done for summer ventilation
between August 30 and September 20, 2006. The mean recovery rate was 100.6% with a coefficient of variation of 10.2% during winter and 106.2% with a coefficient of variation of 13.3% during summer.

At building B, in the summer, methane injection trials were done only when all four 122-cm diameter fans were running. Indeed, ventilation data is considered valid only in these occasions. For the six trials completed between August 10, 2006 and September 14, 2006, the mean recovery rate was 99.4% with a coefficient of variation of 12.0%. For the eleven trials done in winter between January 18 and December 18, 2006, the mean recovery rate was 103.1% with a coefficient of variation of 12.6%.

5.5.2 Precision evaluation of acid traps

The results for all five laboratory trials completed to validate the acid trap set-up are given in table 5.2.

Table 5.2: AMMONIA TRAPPING MEASUREMENTS IN LABORATORY VALIDATION TRIALS

<table>
<thead>
<tr>
<th>Trap identifier</th>
<th>Recovered NH₃ (mg)</th>
<th>Released NH₃ (mg)</th>
<th>Recovery Rate¹ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trial 1, trap 1</td>
<td>1293</td>
<td>1521</td>
<td>85</td>
</tr>
<tr>
<td>Trial 1, trap 2</td>
<td>4</td>
<td>1521</td>
<td></td>
</tr>
<tr>
<td>Trial 2, trap 1</td>
<td>1325</td>
<td>1.58</td>
<td>88</td>
</tr>
<tr>
<td>Trial 2, trap 2</td>
<td>7</td>
<td>1521</td>
<td></td>
</tr>
<tr>
<td>Trial 2, trap 1 rinse</td>
<td>8</td>
<td>1521</td>
<td></td>
</tr>
<tr>
<td>Trial 3, trap 1</td>
<td>1349</td>
<td>1521</td>
<td>90</td>
</tr>
<tr>
<td>Trial 3, trap 2</td>
<td>10</td>
<td>1521</td>
<td></td>
</tr>
<tr>
<td>Trial 3, trap 1 rinse</td>
<td>11</td>
<td>1521</td>
<td></td>
</tr>
<tr>
<td>Trial 4, trap 1</td>
<td>1379</td>
<td>1521</td>
<td>92</td>
</tr>
<tr>
<td>Trial 4, trap 2</td>
<td>11</td>
<td>1521</td>
<td></td>
</tr>
<tr>
<td>Trial 4, trap 1 rinse</td>
<td>14</td>
<td>1521</td>
<td></td>
</tr>
<tr>
<td>Trial 5, trap 1</td>
<td>1413</td>
<td>1521</td>
<td>94</td>
</tr>
<tr>
<td>Trial 5, trap 2</td>
<td>14</td>
<td>1521</td>
<td></td>
</tr>
</tbody>
</table>

¹ Includes ammonia recovered in both traps and rinse acid when applicable

The mass of ammonium found in the second trap was between 0.3 and 1% of the mass found in the first one for all five trials. For trials 2, 3 and 4, the acid trap containers were rinsed respectively with 49, 64 and 48 mL of 0.5 N sulphuric acid in order to assess adsorption on the interior trap walls. The quantity of ammonia found in the rinse of the first trap was between 0.6 to 1% of the mass contained in the first
trap, similar in magnitude to the mass found in the second trap. The mean recovery rate for all trials was 89.9% with a coefficient of variation of 0.039 (3.9%).

Recovery rates increased from 85.3 to 93.8% with consecutive trials. This suggests that adsorption sites may have not been fully saturated after 5 hours of bubbling. Indeed, ammonia could be found in the rinse acid of the first trap on all occasions this was tested. This may explain in part why recovery rates did not attain 100%.

5.5.3 Ammonia emission rates

Ammonia emission rates were measured continuously at building A between February 10 and March 20, 2007. From the 16 available daily profiles, average ammonia emission rates from the building ranged between 271 and 476 g · day⁻¹. All daily profiles presented for building A in figure 5.3 were composed of 84 to 103 ammonia emission rate measurements. A complete ammonia mass balance was done on building A every 14 minutes; yielding a maximum number of 103 possible data points for a given day. Ammonia emission rate measurements were discarded when the difference between ammonia concentration at the inlets and every outlet did not exceed 1 ppm.

![Figure 5.3: Ammonia emissions from building A during winter](image-url)
Average hourly ammonia emission profile relative to hourly exterior temperature for two consecutive days, February 10 and 11 2007, are shown in figure 5.4. The exterior temperature data was obtained for the closest available location to building A, which was 20 km away, from the Canadian meteorological service database (Environment Canada).

The number of animals at building A were recorded weekly and are given in table 5.3.

Table 5.3: NUMBER OF ANIMALS HOUSED IN BUILDING A

<table>
<thead>
<tr>
<th>Date</th>
<th>Mature cows</th>
<th>Heifers and calves</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007-02-12</td>
<td>44</td>
<td>27</td>
<td>71</td>
</tr>
<tr>
<td>2007-02-19</td>
<td>43</td>
<td>31</td>
<td>74</td>
</tr>
<tr>
<td>2007-03-01</td>
<td>37</td>
<td>30</td>
<td>67</td>
</tr>
<tr>
<td>2007-03-05</td>
<td>36</td>
<td>39</td>
<td>75</td>
</tr>
<tr>
<td>2007-03-12</td>
<td>37</td>
<td>38</td>
<td>75</td>
</tr>
<tr>
<td>2007-03-19</td>
<td>36</td>
<td>36</td>
<td>72</td>
</tr>
<tr>
<td>2007-03-26</td>
<td>36</td>
<td>31</td>
<td>67</td>
</tr>
</tbody>
</table>

Considering the floor area of 371 m² and the number of animals, mean ammonia
emission factors and their coefficient of variation are given in table 5.4.

Table 5.4: AMMONIA EMISSION FACTORS FOR BUILDING A DURING WINTER 2007 (FEBRUARY AND MARCH)

<table>
<thead>
<tr>
<th></th>
<th>Per building basis</th>
<th>Per animal basis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g · day⁻¹</td>
<td>µg · m⁻² · s⁻¹</td>
</tr>
<tr>
<td>mean</td>
<td>390</td>
<td>12.2</td>
</tr>
<tr>
<td>range</td>
<td>271-476</td>
<td>8.5-14.9</td>
</tr>
<tr>
<td>CV in %[¹]</td>
<td>16</td>
<td>16</td>
</tr>
</tbody>
</table>

[¹] Coefficient of variation

Field measurements at building B took place between May 30 and September 30, 2007 inclusively. Average daily ammonia concentrations for fan 1 was obtained for 24-hour periods with the acid traps while ventilation data was measured continuously. The mass of ammonia measured in the second trap in series was always below the minimum resolution of the apparatus used to complete the titrations. This suggests that with the acid trap set-up and the 9-12 L · min⁻¹ sampling flowrates used, ammonia was completely transferred from the air bubbles to the acid in the first trap. Corresponding data is shown in table 5.5. Also, the proportion of ventilation data where sufficient vacuum was maintained within the building by the fans are shown for every ammonia concentration field measurement in table 5.5.

Between July 5 and August 8, 2007, average daily airflow rate of fan 1 increased by 28%. Indeed, major servicing on fan 1 and 2 occurred on July 12, 2007. Both fans were therefore recalibrated with their corresponding anemometer to take in account changes in performance.

The number of animals housed in building B, presented in table 5.6, were recorded every time the acid traps were installed. These values were used to calculate the emission factors on a per animal basis.

Mean daily ammonia emission from building B during the summer of 2007 was 1175 g · day⁻¹ with a coefficient of variation of 16%. Considering the housing area of 1022 m², ammonia emissions ranged between 10.51 and 16.04 µg · m⁻² · s⁻¹. On a per animal basis, mean ammonia emission was 14.27 g · day⁻¹ with a coefficient of variation of 18%. The contribution from goats and horses to ammonia emissions was considered negligible when expressing them on a per-animal basis since these animals are fed low-protein diets. The caprine animals housed in the buildings were mostly kids.
Table 5.5: GASEOUS AMMONIA CONCENTRATION AND CORRESPONDING VENTILATION MEASUREMENTS AT BUILDING B

<table>
<thead>
<tr>
<th>Date</th>
<th>Gaseous [NH₃]</th>
<th>Airflow Rate [¹]</th>
<th>Ammonia emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(ppm vol)</td>
<td>(m³ • h⁻¹)</td>
<td>(m³ • h⁻¹)</td>
</tr>
<tr>
<td></td>
<td>(µg • m⁻² • s⁻¹)</td>
<td></td>
<td>g • day⁻¹ • animal⁻¹</td>
</tr>
<tr>
<td>May 30-31 2007</td>
<td>1.22</td>
<td>20004</td>
<td>63675[74.5]</td>
</tr>
<tr>
<td>August 8-9 2007</td>
<td>0.78</td>
<td>25581</td>
<td>76710[50.0]</td>
</tr>
<tr>
<td>August 14-15 2007</td>
<td>0.89</td>
<td>25582</td>
<td>76682[53.9]</td>
</tr>
<tr>
<td>August 28-29 2007</td>
<td>0.66</td>
<td>25765</td>
<td>76944[55.8]</td>
</tr>
<tr>
<td>September 27-28 2007</td>
<td>1.05</td>
<td>24894</td>
<td>75371[43.3]</td>
</tr>
</tbody>
</table>

[¹] Normal conditions, 0°C and 100 kPa
[²] Proportion in % of ventilation data where building was under sufficient vacuum conditions

Table 5.6: NUMBER OF ANIMALS HOUSED IN BUILDING B

<table>
<thead>
<tr>
<th>Date</th>
<th>Mature cows</th>
<th>Replacement animals</th>
<th>Total</th>
<th>Equine</th>
<th>Caprine</th>
<th>Total</th>
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</thead>
<tbody>
<tr>
<td>2007-05-31</td>
<td>72</td>
<td>42</td>
<td>114</td>
<td>0</td>
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<td>4</td>
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<tr>
<td>2007-06-07</td>
<td>65</td>
<td>34</td>
<td>99</td>
<td>0</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>2007-08-08</td>
<td>66</td>
<td>26</td>
<td>92</td>
<td>0</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>2007-08-14</td>
<td>23</td>
<td>35</td>
<td>58</td>
<td>3</td>
<td>16</td>
<td>19</td>
</tr>
<tr>
<td>2007-08-15</td>
<td>54</td>
<td>33</td>
<td>87</td>
<td>0</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>2007-08-21</td>
<td>21</td>
<td>33</td>
<td>54</td>
<td>4</td>
<td>16</td>
<td>20</td>
</tr>
<tr>
<td>2007-08-28</td>
<td>19</td>
<td>32</td>
<td>51</td>
<td>3</td>
<td>18</td>
<td>21</td>
</tr>
<tr>
<td>2007-09-07</td>
<td>20</td>
<td>35</td>
<td>55</td>
<td>3</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>2007-09-20</td>
<td>69</td>
<td>36</td>
<td>105</td>
<td>4</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td>2007-09-28</td>
<td>69</td>
<td>36</td>
<td>104</td>
<td>4</td>
<td>9</td>
<td>13</td>
</tr>
<tr>
<td>2007-10-05</td>
<td>69</td>
<td>36</td>
<td>105</td>
<td>4</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>2007-10-12</td>
<td>68</td>
<td>38</td>
<td>106</td>
<td>4</td>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td>2007-10-15</td>
<td>68</td>
<td>38</td>
<td>106</td>
<td>4</td>
<td>10</td>
<td>14</td>
</tr>
</tbody>
</table>
Ammonia emission rates expressed on a per animal basis for both buildings in this study are within the wide range found in the literature: 0.1625 g · day\(^{-1}\) · AU\(^{-1}\) in Austria [Amon et al., 2001] to 23.38 g · day\(^{-1}\) · animal\(^{-1}\) (974 mg · h\(^{-1}\) · animal\(^{-1}\)) in Western Europe [Groot Koerkamp et al., 1998], where 1 AU (animal unit) is equivalent to 500 kg of live weight. This was also true for ammonia emission rates expressed on a building surface area basis in Minnesota: 0.18 to 196 μg · m\(^{-2}\) · s\(^{-1}\) [Gay et al., 2003; Zhu et al., 2000]. However, some of the values given by Groot Koerkamp et al. [1998] and Amon et al. [2001] reflect annual values or only winter values, those given by Gay et al. [2003] are from 20-minute long punctual measurements at several locations in the summer, while those given by Zhu et al. [2000] are from punctual daytime measurements, 7 over a 12-hour period, at one location. Care must be taken when comparing daily ammonia emission rates from several studies on dairy livestock buildings. Indeed, several parameters such as methodologies used, livestock management practices, feed rations, climate, building configuration and types of floors can have an incidence on measured ammonia emission rates. This explains the wide range of ammonia emission rates found in the literature. Even the units used to express ammonia emission rates can thwart comparisons. In this case, summer ammonia emissions from building B would appear to be of similar magnitude to winter emission rates from building A when expressing them on a floor area basis: 10.51 to 16.04 μg · m\(^{-2}\) · s\(^{-1}\) and 8.46 to 14.9 μg · m\(^{-2}\) · s\(^{-1}\). This can be explained by the lower density of animals contained in building B since part of the herd is sent outdoors during the summer. On the other hand, the ammonia emission rate expressed on a per animal basis for building B during summer, 11.33 to 18.20 g · day\(^{-1}\) · animal\(^{-1}\), would appear higher than the ammonia emission rates for building A during winter, 3.77 to 6.80 g · day\(^{-1}\) · animal\(^{-1}\).

### 5.6 Conclusion

In this paper, ammonia emission rates from two tie-stall dairy livestock buildings in Canada were measured. Building A was monitored continuously during February and March 2007. A complete ammonia mass balance could be performed on the building every 14 minutes by sequentially sampling air from every fan outlet and two air inlets and by continuously measuring the ventilation flow rate at every fan. From the 16 available daily profiles, average ammonia emission rates at building A ranged between 8.46 and 14.9 μg · m\(^{-2}\) · s\(^{-1}\). On the other hand, daily ammonia emission rates were successfully measured at building B on six occasions between May and September 2007 and ranged from 10.51 to 16.04 μg · m\(^{-2}\) · s\(^{-1}\). Daily emission profiles were not available at building B since acid traps were used to measure airflow ammonia concentrations for 24-hour periods at one representative fan. This would yield an average ammonia concentration at a given fan for the whole sampling period, which would
then be extrapolated to the whole building using the buildings average daily ventilation rate. This was done because high summer ventilation rates diluted the ammonia content in the air to a point where it was below the resolution of the ammonia analyser installed.

The acid traps' precision was evaluated in the laboratory using a standard gas mixture of ammonia and air. The average ammonia recovery rate was 89.9% with a coefficient of variation of 3.89%. Recovery rates increased with consecutive trials, which suggests that ammonia adsorption sites were not completely saturated after several hours of experimentation even though several precautions were taken to limit desorption between trials.

The precision of ventilation measurements for each building was also assessed indirectly by injecting known quantities of methane in the building and measuring its recovery rate thru the air sampling system connected to a methane infrared analyzer. Ventilation measurements were done by calibrated free-running propeller anemometers installed in-line with the fans present in both buildings. The anemometers were calibrated in a chamber style wind tunnel conforming to ANSI/ASHRAE 51-1999 (2000) standards. At building B, during summer, average methane recovery rate for 6 completed trials was 99.4% with a coefficient of variation of 12.0%. At building A, during winter, average methane recovery rate was 100.6% with a coefficient of variation of 10.2%.

The ammonia emission rates measured at both farms on a per-animal basis are within the range of measurements found in the literature; 0.1625 g · day$^{-1}$ · AU$^{-1}$ in Austria [Amon et al., 2001] to 23.38 g · day$^{-1}$ · animal$^{-1}$ (974 mg · h$^{-1}$ · animal$^{-1}$) in Western Europe [Groot Koerkamp et al., 1998]. Indeed, daily ammonia emission rates at building B in the summer ranged from 11.33 to 18.20 g · day$^{-1}$ · animal$^{-1}$ and those measured at building A in the winter ranged from 3.77 to 6.80 g · day$^{-1}$ · animal$^{-1}$.

5.7 Acknowledgments

The authors wish to acknowledge the initiative and financial support of GAPS (Information Gaps in Water Quality and Nutrients) from Agriculture and Agrifood Canada. They would also like to thank the owners of both commercial farms, Mr. Jean-Noël Groleau and Mr. Marcel Roy, and Mr. Serge Bérubé from University of Sherbrooke for his technical collaboration to the project.
Article bibliography


CONCLUSION

Ammonia emission rate measurements conducted in this study are presented in the following table.

<table>
<thead>
<tr>
<th>Infrastructure</th>
<th>Measurement period</th>
<th>Average ammonia emission rate</th>
<th>Coefficient of variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dairy Livestock building A</td>
<td>February 10 to March 20 2007</td>
<td>5.47 g·day(^{-1})·animal(^{-1})</td>
<td>18</td>
</tr>
<tr>
<td>Dairy Livestock building B</td>
<td>May 30 to September 28 2007</td>
<td>14.19 g·day(^{-1})·animal(^{-1})</td>
<td>20</td>
</tr>
<tr>
<td>Swine manure storage</td>
<td>May to November 2007</td>
<td>0.071 µg·m(^{-2})·s(^{-1})</td>
<td>71</td>
</tr>
<tr>
<td>Dairy manure storage (frozen)</td>
<td>January 23 to March 3 2007</td>
<td>6.5 µg·m(^{-2})·s(^{-1})</td>
<td>76</td>
</tr>
<tr>
<td>Dairy manure storage (unfrozen)</td>
<td>August 15 to December 31 2006</td>
<td>140 µg·m(^{-2})·s(^{-1})</td>
<td>16</td>
</tr>
</tbody>
</table>

The dairy manure storage cover was less air-tight than the swine manure cover due to structural modifications completed on the dairy manure storage cover. This is probably the main cause of higher ammonia emissions from the dairy manure storage. Ammonia emissions from the latter were significantly higher when the manure surface was unfrozen; which was expected. Indeed, as observed in the preceding table, the dairy storage emitted 6.5 µg·m\(^{-2}\)·s\(^{-1}\) of ammonia when frozen and 140 µg·m\(^{-2}\)·s\(^{-1}\) when unfrozen. On the other hand, the swine manure storage emitted negligible amounts of ammonia, 0.071 µg·m\(^{-2}\)·s\(^{-1}\) on average, indicative of the structural integrity of the cover. Indeed, the equilibrium between surface ammonia concentration and ammonia concentration in the gas underneath the cover yet above the manure surface was not disrupted by large amounts of ammonia-free air.

As for the dairy livestock buildings, ammonia emission rates were higher in summer (14.19 g·day\(^{-1}\)·animal\(^{-1}\)), than in winter (5.47 g·day\(^{-1}\)·animal\(^{-1}\)). Increased ammonia emission rates at higher temperatures is expected. However, these measurements were taken from different livestock buildings with different equipment. It would have been interesting to measure ammonia emission rates from the same building over several seasons with the same procedure. However, the availability or lack thereof of an infrastructure or measurement equipment is often the tradeoff when performing large-scale studies instead of pilot or laboratory scale studies.
Precise building ventilation flowrate measurements with propeller anemometers has its challenges. However, the availability of a chamber-style wind tunnel to calibrate these pieces of equipment made it possible to achieve acceptable precision.

Considering the high variability in emission rates reported in the literature and the effort it took to evaluate the precision of the equipment used for ammonia concentration measurements, further study on ammonia's reactivity with dust, humidity, tubing material is required in the future. Indeed, the latter factors affect the precision of ammonia concentration measured by several sensors.

Also, going at great lengths to conserve ammonia during storage only to have it volatilize by using improper manure spreading equipment such as high jet nozzles is unsound. Limiting ammonia volatilisation throughout the complete life cycle of manure, from animal excretion to spreading, must be achieved to maintain manure's fertilizer value. Therefore, adding an experimental phase on ammonia losses during manure spreading to cover the whole life cycle would provide an interesting avenue for future studies.

Regardless, this study still breaks the ice for the development of ammonia emission factors for Canadian agriculture. Indeed, studies from the United States of America and Western Europe only were actually available for this purpose. The emission rates measured from the two dairy livestock buildings and the covered manure storages were generally lower than those measured in the latter geographical areas.
GLOBAL BIBLIOGRAPHY


