

Methane and nitrous oxide emissions from Canadian animal agriculture: A review

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Kebreab, E., Clark, K., Wagner-Riddle, C. and France, J. 2006. **Methane and nitrous oxide emissions from Canadian animal agriculture: A review**. *Can. J. Anim. Sci.* **86**: 135–158. Considerable evidence of climate change associated with emissions of greenhouse gases (GHG) has resulted in international efforts to reduce GHG emissions. The agriculture sector contributes about 8% of GHG emissions in Canada mostly through methane (CH₄) and nitrous oxide (N₂O). The objective of this paper was to compile an integrative review of CH₄ and N₂O emissions from livestock by taking a whole cycle approach from enteric fermentation to manure treatment and storage, and field application of manure. Basic microbial processes that result in CH₄ production in the rumen and hindgut of animals were reviewed. An overview of CH₄ and N₂O production processes in manure, and controlling factors are presented. Most of the studies conducted in relation to enteric fermentation were in dairy and beef cattle. To date, research has focussed on GHG emissions from the stored manures of dairy, beef cattle and swine; therefore, we focus our review on these. Several methods used to measure GHG emissions from livestock and stored manure were reviewed. A comparison of methods showed that there were agreements between most of the techniques but some systematic differences were also observed. Additional studies with comprehensive comparisons of methodologies are needed in order to allow for comparison of results obtained from studies using contrasting methodologies. The need to standardize measurement methods and reporting to facilitate comparison of results and data integration was identified. Prediction equations are often used to calculate GHG emissions. Various types of mathematical approaches, such as statistical models, mechanistic models and estimates calculated from emission factors, and studies that compare various types of models are discussed herein. A lack of process-based models describing GHG emissions from manure during storage was identified. A brief description of mitigation strategies focussing on recent studies is given. Reduction in CH₄ emissions from ruminants through the addition of fats in diets and the use of more starch was achieved and a transient beneficial effect of ionophores was reported. Grazing management and genetic selection also hold promise. Studies focussed on manure treatment options that have been suggested to reduce gas fluxes from manure storage, composting, anaerobic digestion (AD), diet manipulation, covers and solid-liquid separation, were reviewed. While some of these options have been shown to decrease GHG emissions from stored manure, different studies have obtained conflicting results, and additional research is needed to identify the most promising options. GHG emissions from pasture and croplands after manure application have been the subject of several experimental and modelling studies, but few of these have linked field emissions to diet manipulation or manure treatments. Further work focussing on the entire cycle of GHG formation from feed formulation, animal metabolism, excreta treatment and storage, to field application of manure needs to be conducted.

Key words: Greenhouse gases, enteric methane, nitrous oxide, manure management

Kebreab, E., Clark, K., Wagner-Riddle, C. et France, J. 2006. **Émissions de méthane et d'oxyde nitreux par les productions animales au Canada : rétrospective**. *Can. J. Anim. Sci.* **86**: 135–158. Les innombrables preuves indiquant que les émissions de gaz à effet de serre (GES) jouent un rôle dans le changement climatique ont incité la collectivité internationale à prendre des mesures pour réduire de tels dégagements. L'agriculture explique environ 8 % des rejets de GES au Canada, principalement de méthane (CH₄) et d'oxyde nitreux (N₂O). Les auteurs voulaient faire un tour d'horizon complet des émissions de CH₄ et de N₂O attribuables aux productions animales en recourant à l'approche du cycle, c'est-à-dire de la fermentation entérique à l'épandage du fumier après son traitement et son stockage. Ils passent en revue les processus bactériens fondamentaux expliquant la production de CH₄ dans le rumen et l'intestin des animaux puis donnent un aperçu des mécanismes qui engendrent la libération de CH₄ et de N₂O par le fumier ainsi que des facteurs régulant le phénomène. La majorité des études sur la fermentation entérique se rapportent aux bovins laitiers et aux bovins de boucherie. Jusqu'à présent, les recherches se sont concentrées sur les rejets de GES par le fumier des bovins et des porcins durant son entreposage; c'est pourquoi les auteurs s'y sont attardés. On recourt à diverses méthodes pour mesurer les émissions de GES des animaux et des stocks de fumier. Lorsqu'on compare ces dernières, on constate une concordance générale dans la plupart des cas, mais aussi quelques écarts systématiques. On a besoin d'études supplémentaires comparant les diverses méthodes pour mettre en opposition les résultats issus d'études qui recourent à des méthodes contrastantes.

Abbreviations: AD, anaerobic digestion; ADF, acid detergent fibre; bLS, backwards Lagrangian stochastic; DEI, digestible energy intake; DM, dry matter; DMI, dry matter intake; EF, emission factor; fDF, fermentable dietary fibre; GE, gross energy; GHG, greenhouse gas; GWP, global warming potential; IHF, integrated horizontal flux; IPCC, International Panel on Climate Change; ME, metabolizable energy; MMB, micrometeorological mass balance; NDF, neutral detergent fibre; NFC, nonfibre carbohydrate; RFI, residual feed intake; TDL, tunable diode laser; TS, total solids; VFA, volatile fatty acids

Les auteurs estiment que les méthodes de mesure et de déclaration doivent être normalisées pour que les résultats se comparent plus aisément et qu'on intègre mieux les données. On fait souvent appel à des équations de prévision pour calculer les émissions de GES. Les auteurs examinent diverses approches mathématiques comme les modèles statistiques, les modèles mécanistes et les estimations reposant sur les facteurs de dégagement ainsi que les études comparant différents modèles. Les auteurs déplorent l'absence de modèles articulés sur les processus pour décrire les émissions de GES du fumier durant son entreposage. Ils décrivent brièvement les stratégies d'atténuation en insistant sur les études les plus récentes. L'addition de lipides à la ration et un plus grand usage de l'amidon réduisent la production de CH₄ par les ruminants; on signale aussi un effet bénéfique passager pour les ionophores. La gestion de la paissance et l'amélioration génétique sont deux autres méthodes prometteuses. Les auteurs passent en revue les recherches sur divers conditionnements du fumier susceptibles d'aboutir à une réduction des flux de gaz par stockage, compostage, fermentation anaérobie, adaptation de la ration, usage d'une couverture et séparation des phases liquide et solide. Bien que certaines de ces solutions diminuent les rejets de GES du fumier durant l'entreposage, d'autres études aboutissent à des résultats contradictoires. Il faudrait donc entreprendre d'autres recherches afin d'identifier les options les plus prometteuses. Les dégagements de GES des pâturages et des cultures après application de fumier ont aussi fait l'objet de plusieurs études expérimentales ou de modélisation, mais on a rarement établi un lien entre les gaz émis par les terres et la modification du régime ou le conditionnement du fumier. Les auteurs croient qu'il faudrait effectuer d'autres recherches sur le cycle complet des GES, en prenant en compte la formulation des aliments du bétail, le métabolisme des animaux, le traitement et le stockage des excréments ainsi que la bonification des terres par l'épandage de fumier.

Mots clés: Gaz à effet de serre, méthane entérique, oxyde nitreux, gestion du fumier

Greenhouse gases (GHG) are atmospheric gases that absorb and re-emit long-wave radiation released by the earth back to the surface and include carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O). For about 1000 yr before the industrial revolution, the amount of GHG in the atmosphere remained relatively constant. Since then, the concentration of various GHG has increased, which is at least partly attributed to anthropogenic sources. The amount of CO₂, for example, has increased by more than 30% since pre-industrial times and is still increasing at an unprecedented average rate of 0.4% yr⁻¹ (Intergovernmental Panel on Climate Change 2001). The consequence of the increases in GHG is a rise in average global temperature (0.5–2.5°C by 2030) with concomitant rise in global mean sea level predicted to be in the range of 17–26 cm by 2030. This will affect water supplies, distribution of deserts and wet areas, the range and number of pests that affect plants or diseases, and biodiversity (Moss et al. 2000). Globally, 360 Mt of CH₄ and between 10 and 17.5 Mt of N₂O are released from anthropogenic sources annually (Olsen et al. 2003). In 2002, Canada contributed 4.5 Mt of CH₄ and 0.17 Mt of N₂O and 576 of Mt CO₂ to global emissions, for a total of ~730 Mt CO₂-equivalent (Matin et al. 2004). CO₂-equivalent is a measure used to compare the emissions from various GHGs based on their global warming potentials (GWP). The GWP of CO₂, CH₄ and N₂O used by Environment Canada (2005) [quoting IPCC (1996)] are 1, 21 and 310, respectively. However, IPCC (2001) lists the 100-yr GWP values of CH₄ and N₂O as 23 and 296, respectively.

Globally, agriculture accounts for about one-fifth of the projected anthropogenic greenhouse effect – producing about 50 and 70%, respectively, of overall anthropogenic CH₄ and N₂O emissions. Agricultural activities (not including forest conversion and biomass burning) are estimated to account for approximately 5% of anthropogenic emissions of CO₂ (IPCC 2001). The largest biogenic sources of CH₄ are enteric fermentation from ruminant animals (16%) and rice production (11%) (IPCC 2001). Other sources include landfills, natural wetlands, biomass burning, oceans, and

insects (Crutzen 1991). The main human-related sources of N₂O are agricultural soil management, mobile and stationary combustion of fossil fuel, adipic acid production, and nitric acid production. N₂O is also produced naturally from a wide variety of biological sources in soil and water. On a global basis, it is estimated that natural sources account for over 60% of the total N₂O emissions (IPCC 2001).

In 2002, agriculture-related GHG emissions totalled 59 Mt CO₂-equivalent, and contributed 8% of total national emissions in Canada. This sector accounted for 65% of Canada's total emissions of N₂O and 26% of CH₄ emissions.

Livestock Contributions to Emissions

Greenhouse gas emissions from the agricultural sector that are related to animal production comprise CH₄ directly emitted from domestic animals, CH₄ and N₂O emitted from manure and grazed lands, and N₂O emitted from soils after application of manure (Fig. 1). On a category basis, domestic animals are estimated to contribute directly 32% (19 Mt CO₂-equivalent) of Canadian agricultural emissions, manure management 17% (10 Mt CO₂-equivalent) and soils 50% (30 Mt CO₂-equivalent), which is in part associated with manure addition to crops or pasture (Matin et al. 2004). Hence, animal production is related to more than half of the Canadian agricultural GHG emissions representing an important source for the sector. Ruminants (especially beef and dairy cattle) are mainly responsible for enteric emissions of CH₄ with a minor contribution from large monogastrics (swine). This review concentrates on the major sources indicated above.

Canada's commitment under the Kyoto Protocol is to reduce net GHG emissions to 6% below 1990 levels of 608 Mt by 2008–2012. As the Protocol came into effect on 16 February 2005, the Government of Canada has made climate change a national priority, and its commitment to climate change action since Budget 2000 totals \$3.7 billion (Environment Canada 2005). Given the importance of livestock-related GHG contribution, there is potential for

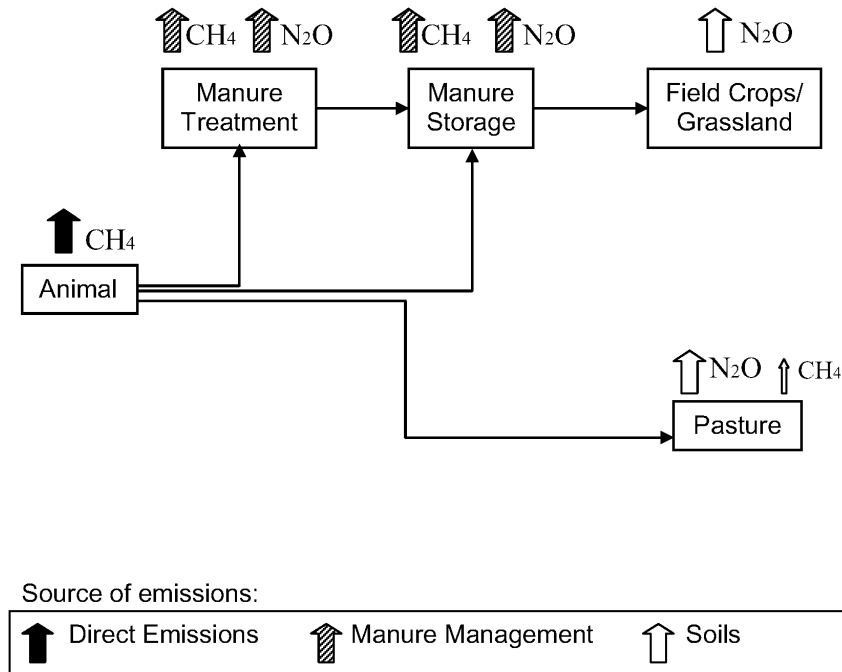


Fig. 1. Flow of manure from animal to fields and sources of CH₄ and N₂O emission associated with components of animal production. Methane from pasture is negligible.

Beneficial Management Practices that span animal production, manure management and field application of manure to mitigate Canadian agricultural emissions. However, in order for the agriculture sector to achieve its potential in contributing to Canada’s climate change commitments, a multi-disciplinary effort comprising expertise in animal nutrition, atmospheric science, plant science, engineering, soil science and mathematics is needed. These efforts must address all components shown in Fig. 1, as well as interactions between components.

Objective

The objective of this paper is to review CH₄ and N₂O emissions related to livestock production holistically by considering emissions from enteric fermentation, manure management and soils. Processes involved in GHG production, methods of measurement, mathematical models for estimation and an update of mitigation practices are discussed here with the goal of identifying areas where livestock production in Canada can reduce its impact on climate change. The focus of the review is emissions from enteric fermentation in ruminants, and from stored manure from ruminants and swine.

METHANE FROM ENTERIC FERMENTATION

Overview of Processes

About 90% of CH₄ emissions from enteric fermentation in Canada (19 Mt CO₂-equivalent, 3% of total GHG emissions) comes from ruminants (Matin et al. 2004). Enteric CH₄ production arises principally from microbial fermentation of hydrolysed dietary carbohydrates such as cellulose,

hemicellulose, pectin and starch. Energy for microbial growth on organic matter in anaerobic environments is derived from substrate oxidation, involving electron transfer to acceptors other than oxygen (O₂) (derived from substrate). Such processes (“fermentations”) occur in the intestinal tract of ruminants (rumen) and non-ruminants (caecum) and in stored manure (Demeyer and Van Nevel 1975). The primary substrates for ruminal methanogenesis are hydrogen (H₂) and CO₂. Most of the H₂ produced during fermentation of hydrolysed dietary carbohydrates, much of which is generated during the conversion of hexose to acetate or butyrate via pyruvate, ends up in CH₄. Significant quantities of ruminal CH₄, particularly with high-protein diets, can also arise from microbial fermentation of amino acids, the end-products of which are ammonia, volatile fatty acids (VFA), CO₂ and CH₄ (Mills et al. 2001).

The amount of CH₄ produced by an animal is influenced by many factors. These include dietary factors such as type of carbohydrate in the diet, level of feed intake, level of production (e.g. annual milk production in dairy), digesta passage rate, presence of ionophores, degree of saturation of lipids in the diet, environmental factors such as temperature (McAllister et al. 1996) and genetic factors such as efficiency of feed conversion (Nkrumah et al. 2006). These factors are discussed later in relation to mitigating strategies for reducing CH₄ emissions from ruminants. Table 1 summarises measured CH₄ output from dairy and beef cattle experiments carried out in North America. The range reported was 8.9 to 21.4 MJ d⁻¹ animal⁻¹. In general, CH₄ production is positively correlated with DMI and level of production in dairy cattle.

Table 1. Methane emissions (per head) by different types of cattle from selected experiments conducted in North America^z

Type of animal	Body weight (kg)	Number of animals	Lactation ^y	Milk (L d ⁻¹)	DMI (kg d ⁻¹) ^x	CH ₄ (MJ d ⁻¹) ^w	Method of measurement	Source
Dairy	–	8	NL	–	6.7	8.9	Respiration mask	Belyea et al. (1985)
Dairy (Holstein)	310	6	NL	–	8.2	9.5	Tracer gas (SF ₆)	Boadi and Wittenberg (2002)
Beef (Charolais × Simmental)	310	6	NL	–	8.4	9.5	Tracer gas (SF ₆)	Boadi and Wittenberg (2002)
Steers (Red Angus)	345	8	NL	–	11.1	11.4	Tracer gas (SF ₆)	Boadi et al. (2002b)
Dairy (Holstein)	–	36	L	32	25.2	21.4	Tracer gas (SF ₆)	Johnson et al. (2002)
Dairy (Holstein)	602	118	L	29	17.5	20.3	Infrared gas analyser from barn	Kinsman et al. (1995)
Beef (Hereford-Simmental)	511	16	L	–	11.4	13.7	Tracer gas (SF ₆)	McCaughy et al. (1999)
Steers	356	16	NL	–	13.2 – 14.9	8.9–11.3	Tracer gas (SF ₆)	McCaughy et al. (1997)
Dairy (Holstein)	–	88–109	L	31	16.1	20.7	Infrared gas analyser from barn	Sauer et al. (1998)
Beef (Holstein)	312	16	NL	–	7.4	9.1	Chamber	McGinn et al. (2004)

^zWhere possible, information from control animals in the experiments is given.

^yL = lactating, NL = non-lactating.

^xDMI = dry matter intake.

^wA mole of CH₄ (= 16 g) is assumed to give 2.1 kcal of energy.

Methods of Measuring Enteric Fermentation

Several methods have been used to measure CH₄ emissions from livestock, largely ruminants. These range from building an elaborate chamber with various types of gas analysers to tracer techniques and whole-barn mass-balance techniques. Johnson and Johnson (1995) give a critical review of some of the methods used; therefore, attention is given here to the most commonly used techniques and studies providing a comparison of methods.

Respiration Chamber (Calorimeter)

Respiration chambers have been used to collect and analyze various gases including CH₄ from animals. The technique is based on the first law of thermodynamics and involves measurement of the volume of gases leaving the chamber. Typically chambers are constructed of steel with an air conditioning system to provide environmental control within a temperature range of 18 ± 2°C and relative humidity of 60 ± 10%. Gaseous composition of the ingoing and outgoing air from the respiration chamber can then be measured using various methods such as dual-channel infra-red and paramagnetic analysers (Cammell et al. 1986; McLean and Tobin 1987). Despite the accuracy of measurement, the expense of construction and operation of a respiration chamber, and inapplicability to animals at pasture limit the use of this method.

Portable Analyser

As a modified version of the respiration chamber, Kelly et al. (1994) describe development of a portable, open-circuit indirect calorimetry system, which can be used to measure CH₄ emissions from sheep and cattle. The system is based on O₂, CO₂ and CH₄ analysers mounted on a cart for ease of

mobility. Absolute pressure and air flow are also measured. The animal is trained to enter the controlled system through a hood from which the gases are sucked and passed through the analysers (Kelly et al. 1994). A slight negative pressure is maintained inside the hood to prevent gases leaving the system through the hood opening. McBride and Odongo (2004) automated the system and were able to take measurements at 10-s intervals, while watching the behaviour of the animal through a webcam. Newer technology provided the means to detect slight changes in CH₄ concentrations and they further modified the system to measure air flow more accurately and were able to suck air from the hood at rates above 600 L min⁻¹. The main disadvantages to this technique are the high labour cost to train and monitor the animals, the inability to measure fully hindgut methane and the restriction that the method cannot be used on pasture.

Polythene Tunnel

The system is constructed using a large polythene tunnel with two small wind-tunnels used to blow air into, and draw air from the larger tunnel. Concentration of CH₄ in air entering and leaving the tunnel is measured using a gas chromatograph fitted with a flame ionization detector [detailed description is provided by Lockyer and Jarvis (1995)]. Murray et al. (1999), using the same system, reported that a CH₄ concentration rise to about 10 mL L⁻¹ in the tunnel can be detected with an accuracy of about 0.4% over the measurement range. The advantages of the system are that it allows free movement of animals inside the tunnel and is inexpensive to build. However, control of temperature inside the tunnel during high ambient temperatures is challenging. Due to space limitations, most experiments using this method have been limited to sheep.

Isotope Dilution Technique

An isotope dilution technique based on continuous infusion of radioactively labelled CH_4 into the animal so as to achieve mixing with CH_4 in solution in the rumen fluid was described by Murray et al. (1976). After equilibrium is reached, the specific activity of CH_4 in the gas phase, which is directly derived from the pool in solution, indicated the rate of ruminal production of CH_4 (Murray et al. 1976). France et al. (1993) reported a number of compartmental schemes for estimating ruminal methanogenesis from isotope tracer dilution data under steady and non-steady-state conditions. Tracer administration by constant infusion and single dose injection were both given consideration, and calculations for estimating VFA production from methanogenesis were also provided (France et al. 1993). The technique generally requires simple experimental designs, and user-friendly software such as WinSAAM[®] is available for calculations. However, difficulty in preparation of the infusion solution due to low solubility of CH_4 gas can be a major limitation (Johnson and Johnson 1995).

Gas Tracer Technique

The most commonly used inert gas tracer is sulphur hexafluoride (SF_6). The technique assumes that rate of SF_6 emission is exactly the same as that of CH_4 emission. The technique as described by Johnson et al. (1994b) involves placing a permeation tube containing SF_6 in the rumen, collecting samples from the animal's nose and mouth and determining CH_4 and SF_6 concentrations by gas chromatography. Methane production is then calculated as the ratio of CH_4 and SF_6 concentrations multiplied by release rate of SF_6 from the permeation tube.

The technique is particularly useful for free-ranging cattle because it allows direct CH_4 emission estimates as the animal is grazing at pasture, which in the case of beef cattle could be during 5 to 12 mo per year (McCaughy et al. 1997).

A tracer technique using ethane (C_2H_4) to measure rumen gas kinetics in grazing dairy cows is described by Moate et al. (1997). They reported that C_2H_4 does not have an effect on the rumen fermentation pattern and was not metabolized. They continuously injected C_2H_4 into the rumen and simultaneously collected rumen gas, which was then analysed for C_2H_4 and principal rumen gases such as CH_4 , H_2 , CO_2 , H_2S and O_2 to study gas kinetics in the rumen headspace. Total CH_4 production can be calculated by dividing the proportion of CH_4 by the proportion of C_2H_4 in the collected gas and multiplying the fraction by total C_2H_4 infused into the rumen (Mbanzamihigo et al. 2002).

Limitations to the use of gas tracer techniques include long withdrawal time of animals after the gas has been released, milk produced may need to be discarded and training is required in handling tracer gases. Furthermore, for a tracer technique such as the SF_6 method to work, large upwind sources of CH_4 or SF_6 emissions have to be avoided, wind direction needs to be monitored and sampling cans should be far enough downwind to allow mixing of CH_4 and SF_6 to allow calculation of CH_4 emissions estimates (Johnson et al. 1994c). When calibrating the rate of release

of SF_6 one should consider the differences in mass between SF_6 and CH_4 .

Micrometeorological Mass Balance Technique

A micrometeorological mass difference technique was developed to measure CH_4 production by cattle under pasture and feedlot conditions (Harper et al. 1999). The technique is based on calculation of CH_4 budgets for the area in which the animals were feeding from measurements of wind speed and atmospheric CH_4 concentrations on the upwind and downwind boundaries. The method requires a mobile, high-precision CH_4 gas analyser (Harper et al. 1999). Judd et al. (1999) also used a non-disturbing micrometeorological flux-gradient technique in which sensible heat was used as a tracer of turbulent transfer. The limitation of the method is that measurements are affected by light winds and rapid wind direction changes (Harper et al. 1999). This method requires sophisticated equipment and qualified personnel with in-depth knowledge of air movement. The micrometeorological mass balance (MMB) technique is also used to measure gases from manure and is discussed later in this review.

Comparison of Measurement Techniques

Johnson et al. (1994c) compared CH_4 production by cattle in chambers with values obtained using the SF_6 technique. Although they found CH_4 estimates from the SF_6 technique to be numerically lower (by 7%), the difference was not significant. Boadi et al. (2002a) reported that mean CH_4 production measured by respiration calorimetry and the SF_6 technique did not differ significantly. Also, they did not detect day-to-day variation of CH_4 production with the calorimetry and tracer methods. However, there were significant between-animal differences and the authors therefore warned that with the tracer method, sufficient animals need to be included to detect differences between treatments, and sufficient collection days per animal are required to minimize between-animal variation.

Murray et al. (1976) compared estimates of CH_4 production from total collection (by measuring air flow through a mask and the content of CH_4 in that air) and from the isotope dilution technique. They found that CH_4 production was not significantly different when estimated by the two methods.

Murray et al. (1999) compared CH_4 emissions from sheep housed in either a polytunnel system or a respiration chamber. They found that CH_4 production measured in the respiration chamber (in L kg^{-1} dry matter intake) was 12.9% greater than in the polytunnel system. Given that recovery of added CH_4 was above 95% for both systems and no systematic differences in measurement errors were detected, the authors suggested that differences in CH_4 emissions were due to effects of housing during sample collection.

Comparison of CH_4 emissions from sheep measured by the MMB and SF_6 techniques showed that, on average, the values per animal were very close (11.9 ± 1.5 vs. 11.7 ± 0.4 g CH_4 sheep⁻¹ d⁻¹, respectively) (Leuning 1999). However, on a daily basis there was some between-animal variation particularly with the MMB technique. The relatively high

amount of animals (14 for MMB and 7 for SF₆ measurements) minimized between-animal variation and the average values when expressed per animal were in close agreement between both techniques.

Most of the techniques use specialized equipment for determination of the concentration of CH₄ and other gases less than 1 ppm. For example, Boadi et al. (2002b) used gas chromatography fitted with a flame ionisation detector and an electron capture detector to measure concentrations of CH₄ and SF₆, respectively. Similarly, Murray et al. (1999) used gas chromatography to measure CH₄. For the MMB method, Leuning et al. (1999) used a high precision infrared spectrometer to measure CH₄ concentrations. The chamber and portable analyzer methods also use infrared CH₄ analyzers to measure CH₄ concentration. So the differences in CH₄ estimates are likely due to sampled concentrations rather than inaccuracy of measuring equipment.

The literature suggests that results of measurements done using unconfined animals using various techniques agree with acceptable level of variation. However, the chamber technique, although reliable, might influence emission rates through changing the animal's behaviour. At present, various techniques and equipment are used to measure CH₄ in Canada. Standardization of techniques is required to build a database of emissions from Canadian livestock production, which will allow accurate estimation of CH₄ emissions. The database can then be used as a platform to develop prediction models. There is also a need to standardize measurements taken at different spatial scales especially when used to downscale or upscale emission values.

Modelling Enteric Emissions from Ruminants

Measurement of CH₄ production in animals requires complex and often expensive equipment; therefore, prediction equations are widely used to calculate CH₄ emissions. Some models have been developed specifically to predict CH₄ emissions from animals and others have either been modified or adapted to calculate CH₄ emission from rumen fermentation. At present, estimation of CH₄ emitted from enteric fermentation at a national and global level is through the use of mathematical models. The Intergovernmental Panel on Climate Change (IPCC) publishes guidelines for national GHG inventories (IPCC 1997) that are used for official estimates of CH₄ emissions.

There have been several attempts to formulate mathematical models to predict CH₄ emissions from cattle (Wilkerson et al. 1995) and swine (Kirchgeßner et al. 1991). The models can be classified into two principal groups: statistical models that relate nutrient intake to CH₄ output directly and dynamic mechanistic models that attempt to simulate CH₄ emissions based on a mathematical description of ruminal fermentation biochemistry. This section describes various models available to estimate CH₄ emissions (including the IPCC models) and provides information on studies that compared extant models and evaluated them against observed data.

IPCC Recommended Factors

The IPCC in its revised reference manual (IPCC 1997) outlines methods of estimating CH₄ emissions from enteric fer-

mentation at two levels of detail and complexity (referred as Tier 1 and 2 methods). The Tier 1 method is a simplified approach that relies on default emission factors (EF) drawn from previous studies. Therefore, only readily available animal population data are needed to estimate emissions. For example, for North American dairy cows the estimated EF is 118 kg head⁻¹ yr⁻¹ (Table 2) assuming an average milk production of 6700 kg head⁻¹ yr⁻¹. Emission factors for non-dairy cattle, sheep and goats are also given in Table 2.

The Tier 2 method is a more complex approach that requires country-specific information on livestock characteristics and manure management practices. IPCC (1997) recommends the Tier 2 approach when the data used to develop Tier 1 values do not correspond well with the country's livestock and manure management conditions. It is also recommended for countries with large cattle populations because cattle characteristics vary significantly from country to country. In Tier 2, average daily feed intake (in terms of energy content, MJ d⁻¹) and CH₄ conversion rates are used to estimate CH₄ emissions. For example, feed intake in dairy cows is estimated from body weight, average daily weight gain, feeding situation, average daily milk production, average amount of work performed per day, percentage of cows that give birth in a year and feed digestibility. Ominiski et al. (2005) calculated the Tier 2 EF for Canadian livestock and noted it was higher than the Tier 1 estimate in all categories except calves under a year old (Table 2).

Statistical (Empirical) Models

Methane production by ruminants has been predicted using simple equations since the 1930s and 1940s (e.g., Kriss 1930; Bratzler and Forbes 1940). These equations are based on total dry matter intake (e.g., Kriss 1930; Axelsson 1949), digestible carbohydrates (Bratzler and Forbes 1940; Moe and Tyrrell 1979), digestibility and feeding level (Blaxter and Clapperton 1965), and a range of animal and dietary factors (Holter and Young 1992; Yan et al. 2000; Mills et al. 2003). One of the earlier CH₄ prediction models that has been widely used was developed by Blaxter and Clapperton (1965) and is based on dry matter intake and digestibility of diet:

$$\begin{aligned} \text{Methane [kcal (100 kcal of GE)}^{-1}] \\ = 1.3 + 0.112D + L (2.37 - 0.05D), \end{aligned} \quad (1)$$

where GE = gross energy, D = digestibility of GE at maintenance, and L = level of feeding relative to maintenance. A mole of CH₄ (= 16 g) is assumed to give 2.1 kcal of energy. Moe and Tyrrell (1979) related intake of carbohydrate fractions to CH₄ production as follows:

$$\begin{aligned} \text{Methane (MJ d}^{-1}) = 3.38 + 0.51 \text{ NFC} \\ + 2.14 \text{ HC} + 2.65 \text{ C}, \end{aligned} \quad (2)$$

where NFC is nonfibre carbohydrate, HC is hemicellulose and C is cellulose (all in kg d⁻¹). Murray et al. (1978), using the isotope dilution technique, developed the following equation:

Table 2. IPCC Tier 1 and Tier 2 emission factors for CH₄ and N₂O from Canadian animal production

Type of animal/system	GHG	Method		Temp.	Units	
		Tier 1 ^z	Tier 2 ^y			
Enteric	CH ₄				kg CH ₄ head ⁻¹ yr ⁻¹	
Dairy cows		118	126.1			
Dairy heifers		56	72.7			
Beef cows		72	90.4			
Bulls		75	93.5			
Heifers > 1 yr		47	62.9			
Steers > 1 yr		47	56.1			
Calves < 1 yr		47	39.9			
Sheep and goats		8				
Horses		13				
Swine		1.5				
Manure						
Dairy			36	44.1		<15°C
Beef		1	2.5	<15°C		
Swine		10	10.4	<15°C		
Poultry		0.078				
Liquid systems	N ₂ O	0.001			kg N ₂ O-N (kg N) ⁻¹ excreted	
Solid storage		0.02				
Pasture		0.02				

^zTier 1 values for enteric fermentation were taken from Environment Canada (2005) and for manure from Marinier et al. (2004).

^yTier 2 values for enteric fermentation were as reported by Ominski et al. (2005) and for manure are adapted from Marinier et al. (2004) by weighting emission factors for cattle categories (e.g., cow, bull, replacement heifers, calves) by population data for 2003 (Statistics Canada 2003a, b) and represent air temperatures less than 15°C.

$$\text{Methane (L d}^{-1}\text{)} = 2.81 + 0.042 \text{ DOMI}, \quad (3)$$

where DOMI is digestible organic matter intake (g d⁻¹). The authors also reported equations for CH₄ production within the rumen and within the hindgut. Yan et al. (2000) related CH₄ energy produced with digestible energy intake (DEI, MJ d⁻¹), silage ADF intake (S_{ADFI}, kg d⁻¹) as a proportion of total ADF intake (T_{ADFI}, kg d⁻¹) and level of intake [L, multiples of metabolizable energy (ME) intake over maintenance requirement] in a linear regression equation based on measurements from 247 cows and 75 beef cattle offered grass silage-based diets:

$$\text{Methane (MJ d}^{-1}\text{)} = \text{DEI (0.094} \\ + 0.028 \text{ S}_{\text{ADFI}}/\text{T}_{\text{ADFI}}) - 2.453 \text{ (L} - 1\text{)}. \quad (4)$$

An early attempt to model CH₄ non-linearly was made by Axelsson (1949) who derived an equation with a quadratic term in DMI. The model cannot be extrapolated beyond DMI of 15–20 kg d⁻¹ because it predicts maximal CH₄ output at 12.5 kg DMI d⁻¹, and the CH₄ output declines with increasing DMI until emissions become negative at DMI greater than 24 kg d⁻¹:

$$\text{Methane (MJ d}^{-1}\text{)} = -2.07 + 2.63 \text{ DMI} \\ - 0.105 \text{ DMI}^2 \quad (5)$$

Recently, Mills et al. (2003) developed linear and non-linear models and recommended Equation 6 for predicting CH₄ where nutrient description data are limited:

$$\text{Methane (MJ d}^{-1}\text{)} = 5.93 + 0.92 \text{ DMI}, \quad (6)$$

$$\text{Methane (MJ d}^{-1}\text{)} = a - (a + b) e^{-c\text{ME}}, \quad (7)$$

where *a* is the theoretical maximum CH₄ output, *b* is minimum CH₄ output, *c* is a shape parameter, DMI is dry matter intake (kg d⁻¹) and ME is metabolizable energy intake (MJ d⁻¹). Mills et al. (2003) reported that parameter *c* is influenced by acid detergent fibre (ADF) and starch content of the diet, where an increase in the former tends to increase CH₄ output while replacement by starch tends to reverse the effect such that:

$$c = -[0.0011 \times \text{Starch (kg d}^{-1}\text{)}/\text{ADF (kg d}^{-1}\text{)}] \\ + 0.0045. \quad (8)$$

Most of the models show that CH₄ production is highly influenced by DMI. However, Lassey et al. (1997) did not find a good relationship between DMI and CH₄ produced. This is likely because intake was not directly measured in the experiment, but DMI was estimated either using IPCC values or digestibility measurements which might not have been sufficiently accurate.

Dynamic Mechanistic Models

According to Thornley and France (2006), a model constructed by looking at the structure of a system, dividing it into its principal components, and analysing the behaviour of the whole system in terms of its components and their interactions is mechanistic. Dynamic models express the time variable explicitly. Several dynamic, mechanistic models that estimate CH₄ emissions have been developed (e.g., Baldwin et al. 1987; Mills et al. 2001). These models require detailed dietary input and the basis for predicting CH₄ production is that excess hydrogen produced during fermentation is utilized for microbial growth, biohydrogenation of unsaturated fatty acids, and the production of glucogenic VFA. The assumption is made that the remaining hydrogen

is used solely and completely for methanogenesis (Mills et al. 2001).

Several studies have shown that a full assessment of mitigation options requires mechanistic models. For example, Benchaar et al. (2001) applied a mechanistic model to demonstrate effectiveness of different nutritional strategies in reducing CH₄ production from ruminants. Kebreab et al. (2004) developed an integrated model that simulates CH₄, N and P output from ruminants given various types of diets. The model was able to show that enteric CH₄ production can be reduced significantly by dietary manipulation.

Comparison of Models

Various studies have focussed on evaluating CH₄ models for their predictive ability when subjected to an independent data set. Wilkerson et al. (1995) reviewed several statistical models and recommended adoption of the Moe and Tyrrell (1979) equation for dairy cows. Mills et al. (2003) also compared various statistical models from the literature as well as models developed by themselves. The models were subjected to testing with extensive calorimetry data from across the United Kingdom. Although the authors found that the Moe and Tyrrell (1979) model gave reasonable predictions, their own non-linear models not only improved prediction but were also less prone to misapplication than that of Moe and Tyrrell (1979). Linear models gave unrealistically high emission values as DMI increased, while non linear models gave values approaching the theoretical maximum emission, a prediction which is biologically realistic.

Benchaar et al. (1998) compared the predictive ability of two mechanistic and two linear regression models against a database constructed from the literature. Predictions from the linear equations were poor with 42 to 57% of the variation explained by the models. The mechanistic models, on the other hand, explained over 70% of the variation. Kebreab et al. (2006) chose six models, including two linear regression models [from Moe and Tyrrell (1979) and Mills et al. (2003)], a non-linear regression model [from Mills et al. (2003)], IPCC Tier 1 and 2 models [from IPCC (1997)], and a dynamic mechanistic model [from Kebreab et al. (2004)] for predicting CH₄ production and challenged them with North American data. The linear models were recommended for use where nutrient information is limited and within the range in which they were developed. The non-linear model of Mills et al. (2003) could be used for extrapolation beyond the range of data used for developing the model but the mechanistic model was recommended for assessment of mitigation options. The Tier 1 model was found to be adequate for general inventory of CH₄ emissions but the Tier 2 model needed further refinement because prediction accuracy was lower perhaps due to its fixed conversion value of GE to CH₄.

Mitigation Strategies to Reduce Enteric Methane Emissions from Cattle

There have been a number of reviews of this subject (e.g., McAllister et al. 1996; Moss et al. 2000). Recently, Boadi et al. (2004a) extensively reviewed mitigation strategies to reduce CH₄ emissions from dairy cows. Therefore, mitigation strategies will be discussed here only briefly and will

focus on additional studies not covered in the previous reviews.

Addition of Fats

Giger-Reverdin et al. (2003) carried out an analysis of diets from the literature to quantify the influence of dietary fat composition on CH₄ production in dairy cattle. They concluded that the C₈-C₁₆ fatty acid component of ether extract was responsible for reduction in CH₄ and this reduction was proportional to the degree of unsaturation of these fatty acids. In vitro experiments showed that medium chain fatty acids (those with 8 to 16 C chain length, such as lauric and myristic acids) caused a greater reduction in CH₄ production than short (< 8 C) or long (>18 C) fatty acids (Dohme et al. 2000). Addition of coconut oil was found to reduce CH₄ emission without reducing animal performance despite lower DMI in finishing beef heifers (Lovett et al. 2003). The authors argued that this is most likely due to reduced total H₂ supply in the rumen through a reduction of the total amount of ruminally fermented organic matter following defaunation (elimination of protozoa from the rumen), a shift towards propionate production and provision of an alternative H₂ sink through bio-hydrogenation.

Addition of sunflower oil to the diet was found to decrease CH₄ emissions by 21% when corrected for differences in energy intake in Holstein steers (McGinn et al. 2004). However, the authors noted that the 5% addition of fat reduced total tract neutral detergent fibre (NDF) digestibility by 20%. They concluded that use of feed additives in commercial beef cattle will depend on the economic benefits.

Forage-to-concentrate Ratio and Restricted Feed Intake

Lovett et al. (2003) reported that feeding diets of low forage-to-concentrate ratio to finishing beef cattle is an effective means to reduce CH₄ output per kg of liveweight and per kg of carcass gain, and even improve feed conversion efficiency. However, Kirkpatrick et al. (1997) did not find any effect of forage-to-concentrate ratio on the energy retention or CH₄ production of beef cattle. Boadi et al. (2004b) reported that CH₄ production (% GEI) was 20% higher in beef steers from a feedlot fed a low forage-to-grain diet than from steers on a high forage-to-grain diet. The differences could be explained partly by higher DMI in steers fed the low forage-to-grain diet. The authors attributed the lower CH₄ production from a high forage-to-grain diet to the effect of high content of fat in the diet.

Kirkpatrick et al. (1997), using measurements from calorimetry chambers, found that beef cattle on restricted intake had a significantly lower CH₄ production (5.3 vs. 7.9% of GE in restricted and ad libitum fed beef cattle, respectively). Okine et al. (2003) calculated CH₄ emission to be 5% lower in steers with low residual feed intake (RFI), the difference between the ME intake and ME required for maintenance and gain). They suggested that cattle with low and/or negative RFI would produce less CH₄ and manure than cattle with high and/or positive RFI because of reduced DMI but similar performance.

Types of Carbohydrates

It is well established that types of carbohydrates consumed have an effect on CH₄ production. A few studies compared the effect of structural vs. non-structural carbohydrates and found that fibre fermentation increases methanogenesis compared with soluble carbohydrate fermentation (e.g. Moe and Tyrrell 1979). Hindrichsen et al. (2004b) studied CH₄ emissions from the rumen for diets containing different types of carbohydrates including lignified and non-lignified fibre, galactomannan, fructan, sucrose and starch. They reported that lignification reduced CH₄ formation possibly due to reduced nutrient availability for methanogens. Supplements with higher non-cellular polysaccharides (such as guar gum) favoured propionate-forming microbes and therefore diverted H₂ away from methanogens. Sugars tend to promote butyrate formation, at the expense of propionate, which provides H₂ for methanogens and therefore increases CH₄ production (Hindrichsen et al. 2004b). On the other hand, the ratio of lipogenic-to-glucogenic VFA (normally expressed as acetate-to-propionate) with starch is considerably lower than with sugars and results in lower CH₄ production (Mills et al. 2001).

Ionophores and Organic Acids

Ionophores are molecules that entrap cations and attach to the lipid bilayer of the cell membrane of ruminal gram-positive bacteria and protozoa, which force the microbes to expel protons at the expense of ATP causing a depletion of energy and likely death (Russel and Strobel 1989). Ionophores are classified as antibiotics with monensin being the most widely used and studied (Boadi et al. 2004a). According to McGuffey et al. (2001), the net effect is a change in the microbial ecosystem and fermentation dynamics in the rumen resulting in improved efficiency of energy capture and utilization of dietary N. McGinn et al. (2004) also showed that monensin decreased CH₄ emissions by 9% when emissions were corrected for energy intake. Several other experiments have shown the potential effect of ionophores to reduce CH₄ emissions from ruminants. However, the benefits in terms of CH₄ reduction were short lived. Johnson et al. (1994a) using monensin and lasalocid showed that CH₄ suppression was not persistent beyond 16 days of ionophore introduction, probably due to development of resistance by the methanogens in the rumen. The European Union has proposed banning antibiotic growth promoters including monensin in animal feed by 2006 due to discovery of resistance to some antibiotics by humans (FASS 2003).

Castillo et al. (2004) reviewed the use of organic acids (malate and fumarate) for beef cattle as a substitute for monensin. They showed that inclusion of organic acids has the potential to reduce methanogenesis by providing substrate for fumarate-utilizing bacteria that compete with methanogens for the utilization of H₂. However, McGinn et al. (2004) showed that addition of yeast and fumaric acid to diets did not have significant effects on CH₄ emissions.

Genetic Selection

Pinares-Patiño et al. (2004) conducted experiments under controlled grazing conditions to minimize selective feeding

and establish a relationship between herbage maturity and CH₄ emission. Although they observed a relationship between the digestible fraction of cell walls and CH₄ production, most of the variation was due to between-animal differences. They concluded that there are intrinsic animal differences associated with CH₄ production that might be used to select animals for reduced CH₄ emission.

Nkrumah et al. (2006) reported that beef cattle with low RFI produced up to 28% less CH₄ than those with high RFI. The authors suggested that the lower CH₄ production could be related to differences in microbial population in the rumen and the traits could be heritable. If so, beef cattle with lower RFI could be selected for increased energetic efficiency in converting feed to beef with lower energy loss as CH₄.

Grazing Management

Management of a herd under an intensive production system grazing high-quality forage (made possible through maintaining soil fertility) was found to reduce CH₄ emission by up to 22% in beef cattle (DeRamus et al. 2003). The reduction in CH₄ emission was related to better digestibility of high quality forage, which resulted in better efficiency of utilisation, as was observed in higher average daily gain. Soil fertility was maintained through application of ammonium nitrate, phosphorus and potassium (DeRamus et al. 2003). Such intensive grazing management adds ancillary sources of GHG emissions, therefore a holistic approach should be taken in determining the benefits of such practices to reduce CH₄ emission from livestock.

Partitioning Methane Production between Forestomach and Hindgut in Ruminants

Murray et al. (1976, 1978) measured CH₄ emission using the isotope dilution technique and reported that CH₄ produced in the rumen was about 88.7% of total CH₄ produced by the animal. As well, CH₄ produced in the lower digestive tract was largely absorbed and excreted through the lungs. The amount excreted via the rectum was 13.4% of CH₄ produced in the hindgut, although this percentage increased with DMI (Murray et al. 1976, 1978). Hofmeyr et al. (1984) used an open circuit respiration chamber to measure directly CH₄ produced in the hindgut by first measuring total CH₄ emission and then emptying the contents of the reticulorumen of sheep. They reported hindgut CH₄ production was 7–8% of total CH₄ production with significant diet differences, with corn leaf based diets giving higher hindgut CH₄ production than alfalfa based diets. Using the technique of Hofmeyr et al. (1984), Torrent and Johnson (1994) measured CH₄ production from hindgut to be 7.5–12.6% of total CH₄ produced by sheep. Schonhusen et al. (2003) investigated the effects of protozoa on CH₄ production in the rumen and hindgut of calves. They observed that methanogenesis in the rumen, but not in the hindgut, was associated with the development of the protozoa population. Hindrichsen et al. (2004b), using the dynamic simulation model of Mills et al. (2001), also found post-ruminal CH₄ production to be 7.9–10.4% when diets from *in vivo* experiments were used for simulation. The results support the

findings of Mills et al. (2001) who reported an average post-ruminal CH₄ production of 9.1% in cows fed corn based diets.

In general, it appears that the contribution of the hindgut to CH₄ formation is lower than that expected from the contribution of the hindgut to total fibre degradation. This may be related to higher levels of acetogenesis in the hindgut compared with the rumen (De Graeve and Demeyer 1988).

Enteric Emissions by Monogastrics

Total amount of CH₄ production by monogastric animals is low compared with that by ruminants (about 10%, Jensen 1996). In the hindgut of monogastrics, as in the rumen, methanogens use H₂ to reduce CO₂ to CH₄, and non-methanogens use H₂ to reduce CO₂ to acetate, which is absorbed into the blood (Moss et al. 2000). The rate of CH₄ production is much higher in the colon than in the caecum of pigs due a much greater presence of methanogenic bacteria in the colon (Jensen 1996).

Many studies have reported the amount of CH₄ excreted in monogastrics depends on intake of non-starch polysaccharide (e.g. Jensen 1996). Noblet et al. (1989) proposed an equation that predicts methane energy loss by pigs as a function of the digestible NDF content of the diet:

$$\begin{aligned} \text{Methane energy (kcal kg}^{-1} \text{ DM)} \\ = 0.24 \text{ digestible NDF (g kg}^{-1} \text{ DM)}. \end{aligned} \quad (9)$$

Galassi et al. (2004) showed methane energy loss was significantly higher with a high NDF diet (beet pulp) compared with a low NDF diet (wheat), both as an absolute value and as a proportion of energy intake.

Methane production in pigs varies with live weight and diet. In growing pigs it varies from almost zero in piglets to 0.8–1% of dietary fibre intake in 125–150 kg pigs (Noblet and Shi 1994). In adult sows, the variation in CH₄ production is largely due to fibre in the diet. The composition and amount of fermentable dietary fibre (fDF, calculated as the difference between digestible organic matter and the sum of digestible crude protein, crude fat, starch, and sugars) influences the composition of microbiota and the pattern of VFA production in the hindgut in growing pigs, which might affect CH₄ production (Rijnen 2003). There was a linear increase in CH₄ production as fDF in the diet increases:

$$\begin{aligned} \text{Methane (kJ kg}^{-0.75} \text{ d}^{-1}) = -44.4 \\ + 1.2 \text{ fDF (g kg}^{-0.75} \text{ d}^{-1}) (R^2 = 0.86). \end{aligned} \quad (10)$$

Dietary manipulation has been considered a mitigating option to reduce CH₄ and N emissions from monogastric animals. Quiniou et al. (1995), for example, compared two diets with different protein levels and found that CH₄ losses from pigs fed the lower protein diet had lower, but not significantly lower, CH₄ emissions. This may be due to the fact that the low protein diet had a higher NDF content. The authors found significantly higher N losses for the high protein diet, which will affect the amount of substrate available for N₂O formation when the excreta are stored. Möhn et al. (2003) reported that reducing dietary protein by 20% result-

ed in up to 30% lower N excretion, which would ultimately reduce the substrate for N₂O emission when stored. They also found that CH₄ emissions were lower for sows fed corn-based than barley-based diets but CH₄ emissions from the latter can be reduced if the dietary protein content was lowered. Similar results were found for finisher pigs by Atakora et al. (2003).

Further information on GHG emissions from monogastrics is largely lacking. For example, the effects of ionophores, organic acids and enzymes in pigs need to be investigated. Poultry and poultry litter are potential sources of CH₄ and N₂O but published studies dealing with this issue are scarce and CH₄ EF for chickens, hens and turkeys have not even been published by IPCC.

METHANE AND NITROUS OXIDE EMISSIONS FROM STORED MANURE

Manure in Canada can be stored over several months, with an estimated 14% of livestock operations using liquid storage, 69% using solid storage, and 24% using neither system but rather keeping their animals on pasture year-round or spreading manure daily (Statistics Canada 2003a). In this section we discuss factors that affect GHG emissions from stored manure, measurement methods and potential mitigation practices. Emissions associated with manure deposited directly at pasture, or applied to soils are briefly discussed in the following section.

Occasionally some form of manure treatment is used, as in the case of aerobic composting or anaerobic digestion, followed by storage of the processed material (Fig. 1). During storage, manure decomposes and CH₄ and N₂O gases can be released. The Canadian GHG Inventory calculated that GHG emissions from manure accounted for 17% of total national agricultural emissions in 2001 (Olsen et al. 2003). The anaerobic nature of liquid manure systems increases the potential for CH₄ production, and reduces N₂O production, whereas solid storage is estimated to be a significant source of both CH₄ and N₂O (Janzen et al. 1998).

The Farm Environmental Management Survey classifies liquid manure as having less than 5% solids (Statistics Canada 2003a). Farms with animals whose manure has a naturally high moisture content, such as swine, usually use liquid manure systems (86% of swine farms); many of the larger dairy farms also use liquid systems (36% of farms with 47 or more head, vs. 7% with fewer than 47 head) (Statistics Canada 2003a). Liquid manure systems include steel or concrete tanks and earthen basins, and can be with or without a cover, and under or outside a barn. Earthen storage systems are often referred to as “lagoons” in Canada, but should not be confused with “anaerobic lagoons”, which are not simply storage structures systems but systems specifically engineered to treat manure solids (Lory et al. 2004).

Solid storage is classified by the Farm Environmental Management Survey as having greater than 20% solid content, but semi-solid manure (solids content between 5 and 20%) is included with solid manure throughout their report (Statistics Canada 2003a). Solid storage is used mainly on beef operations, small to medium-sized dairy farms, and

poultry operations and includes manure stored in indoor or outdoor bedding packs (e.g. feedlots) or piled on concrete pads with or without covers and run-off containment (Statistics Canada 2003a).

In some cases, emissions from two sources such as enteric fermentation and manure storage may occur from the same location and may not be separated, as shown in Fig. 1. This may be the case for swine and dairy operations where liquid manure is stored below the barn, or for beef feedlots where solid manure storage is occurring at the same place as enteric fermentation. This has implications for the interpretation of measured gas emissions, depending on the measurement method used.

Overview of Methane Production Processes in Manure

Methane forms where methanogenic bacteria are present. Conditions favouring survival of methanogenic bacteria are lack of oxygen, a redox potential below -200 mV, neutral pH, nutrients (N, P, K, S), electron acceptors such as NO_3^- , and a substrate rich in organic matter (Conrad 1989). When simple organic compounds are broken down under anaerobic conditions, CO_2 and CH_4 are produced. However, a series of bacteria must first degrade organic matter into a form that can be used by methanogens. Most methanogens thrive under mesophilic conditions and may be restricted at low temperatures (Jones 1991). Methane loss is controlled not only by its production rate, but also by the rate of oxidation and transport, with losses only occurring if CH_4 is not oxidized (Conrad 1989). If CH_4 production is low and the path of its diffusion is long with oxygen present, oxidation will likely occur and little CH_4 will be released. For example, Hao et al. (2001) found that CH_4 accumulated at the bottom of compost windrows, and concluded that slow transport and higher O_2 concentrations near the surface kept emissions lower than production. Where CH_4 is produced so quickly that it cannot escape by diffusion, bubbles will form and pass through overlying substrate and oxidation will not occur (Whalen 2005). This may occur in liquid manure systems where oxygen is scarce, but crusts present on liquid manure may slow the diffusion of gases and allow some oxidation (Petersen et al. 2005).

Manure characteristics such as total solids (TS) content and NH_3 concentration affect the amount of CH_4 lost from manure. An inverse relationship was established between the solids content of manure and the CH_4 produced, where dilute slurry produced more CH_4 than slurry of high TS (Massé et al. 2003a). Methane production in manure with higher TS was probably inhibited by high ammonia levels (Massé et al. 2003a), which can inhibit the growth of methanogenic bacteria, especially at $\text{pH} > 9$ (Miner et al. 2000). The presence of sulphur in the manure, included in the diet or in bedding, negatively affects the rate of methane production (Hao et al. 2005). Methanogens have been shown to suffer from toxicity to sulphur compounds (Lin et al. 2001) and to be out-competed for carbon resources from sulphate-reducing bacteria in a substrate of hydrogen or acetate, as is the case for manure (Oremland and Polcin 1982). Published Canadian studies that have dealt with fac-

tors that influence CH_4 emission from manure storage are summarized in Table 3. Lack of standards for reporting flux measurements make comparison of results difficult. Laboratory studies often report emissions per "unit of manure" (either on a volume or mass basis), while in situ measurement methods yield a flux density, that is, mass of gas per area and time. Conversion of units is often not feasible as studies do not report or measure ancillary data needed.

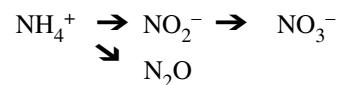
Methane emissions have been shown to increase with air temperature (Kaharabata et al. 1998; Massé et al. 2003a) and are even more closely correlated to manure temperature (Husted 1994; Park et al. 2006). Kaharabata et al. (1998) found an exception to this temperature relationship during nights when wind was not strong enough to mix the air above the tank surface and emissions pooled there.

Rainfall events were also correlated with increased CH_4 loss and were found to increase emission by 1.2–4 times more than the emissions previous to and following rainfall (Kaharabata et al. 1998). This increase in emission was hypothesized to be due to mechanical agitation from the raindrops and low atmospheric pressure allowing easier diffusion of the gas out of the manure.

Storage conditions that affect CH_4 emissions include length of storage, agitation, and emptying. It appears that the longer the manure is stored, the more CH_4 is produced (Massé et al. 2003a). Agitation or mixing of the manure was found to increase CH_4 emissions temporarily, by 2–7 times more than the previous and following days (Kaharabata et al. 1998; Park et al. 2006). Similarly, disturbance caused by emptying tanks led to a nearly immediate but temporary increase of CH_4 . In addition, CH_4 fluxes can be highly variable according to spatial position within a storage tank, and this heterogeneity should be considered when measuring fluxes (Wagner-Riddle et al. 2006).

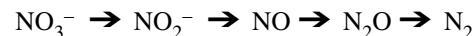
Overview of Nitrous Oxide Production

While there are several pathways of N_2O formation, only nitrification and denitrification will be discussed here, as they are the most significant to production of GHG from manure storage. Nitrification occurs under aerobic conditions and follows two steps where ammonium is first oxidized to nitrite, and nitrite is then converted to nitrate.



N_2O is a by-product of this process. Bacteria involved in nitrification are generally chemoautotrophic and require CO_2 , H_2O , O_2 and either NH_4^+ or NO_2^- for growth, as well as a pH above 5 (Galbally 1989).

Denitrification is the reduction of nitrate to di-nitrogen gas according to:



The process occurs under anaerobic conditions, and nitrogen products are used as the terminal electron acceptor

Table 3. Summary of measured emissions of CH₄ and N₂O from Canadian studies. Standard deviation of mean emissions in parenthesis

Type of manure	Method	Study period	Temperature ^z	Recorded value	Units	Reference
Solid dairy (0–15 cm)	Incubation	Lab, 20 d	22°C	0.162	g N ₂ O-N m ⁻² d ⁻¹	Brown et al. (2000)
(30–60 cm)				–0.001		
Dairy + straw (30–60 cm)						
80% WC ^x						
75% WC				0.237		
70% WC				0.254		
				0.219		
Solid dairy	MMB	1998 Jun. 12–18	–	0.42	g N ₂ O-N m ⁻² d ⁻¹	Brown et al. (2002)
Swine manure	Incubation	Lab, 2 mo storage	–	42.3	g CH ₄ d ⁻¹ m ⁻³	Clark et al. (2005)
Swine slurry	SF ₆ tracer	1995 Jun. 12	–	56 (11.3)	kg CH ₄ m ⁻² yr ⁻¹	Kaharabata et al. (1998)
Dairy slurry		– Nov. 20		74.0 (33.3)		
Swine slurry	Anaerobic digestion	Lab, 26–35 d	10°C	0.080 (0.002)	L CH ₄ (g TCOD _{fed}) ^{-1y}	Massé et al. (2003b)
			15°C	0.218 (0.022)		
			20°C	0.266 (0.014)		
Dairy slurry	Anaerobic digestion (variable TS)	Lab, 180 d	10°C	1.46–2.17	L CH ₄ m ⁻³ d ⁻¹	Massé et al. (2003a)
Swine slurry		Lab, 270 d	15°C	1.06–14.83		
		Lab, 180 d		5.36–30.00		
		Lab, 270 d		4.97–28.08		
Beef feedlot	IHF continuous	2003 Sep. 18 –	–	600.0	g CH ₄ -C (7 d) ⁻¹	Sommer et al. (2004a)
	IHF periodic	Oct. 05		357(12)	g CH ₄ -C (7 d) ⁻¹	
				77(8)	g N ₂ O-N (7 d) ⁻¹	

^zTemp = Temperature of manure.

^yTCOD = total chemical oxygen demand.

^xWC = water content.

instead of oxygen. Nitrous oxide is produced when reduction is incomplete. The conditions necessary for denitrification include the presence of facultative heterotrophic bacteria capable of denitrification, the availability of reductants such as organic carbon, lack of oxygen, and high concentration of NO₃⁻, NO₂⁻ or NO (Firestone and Davidson 1989). This process has been observed at temperatures between 2 and 50°C, but every 10°C rise in substrate temperature may double the rate of denitrification (Galbally 1989). Denitrification will be minimal in fresh manures where NO₃⁻ levels are low, but will increase as NH₄⁺ is oxidized to NO₃⁻ (Mahimairaja et al. 1995). The ratio of N₂O to N₂ produced by denitrification is also affected by pH, moisture content, and N₂O reductase activity (Beauchamp 1997). Mahimairaja et al. (1995) found the ratio of N₂O to N₂ produced in manure to range from 0.09 to 0.21.

Canadian studies that have examined factors affecting N₂O emissions from manure storage systems are summarized in Table 3. Brown et al. (2002) found that the highest daily fluxes of N₂O coincided with the maximum daily temperature. Petersen et al. (1998) found that peaks of N₂O emission from solid manure coincided with increases in air temperature at the beginning of the study, but that this temperature effect was not evident after 3 wk.

N₂O emissions tend to relate directly to the amount of solids in manure. Incorporating straw into manure caused bulk density to decrease and aeration to increase, allowing

for easier diffusion of O₂ into the manure pile and of N₂O out of it (Brown et al. 2000). These authors found that manure water content between 55 and 70% produced the most N₂O, which corresponded to redox potentials between 150 and 250 mV E_v. Nitrification was speculated to be the source at high redox potentials (low water contents) whereas low redox potentials (high water contents) were believed to be associated with N₂O from denitrification (Brown et al. 2000).

N₂O losses due to denitrification have been found to correlate with high nitrate levels (Mahimairaja et al. 1995; Harper et al. 2000) and decreasing NH₄⁺ concentrations, as ammonium was converted to NO₃⁻ (Brown et al. 2000). Manure samples that produced little or no N₂O had low concentrations of nitrate throughout the incubation and high levels of NH₄⁺ (Brown et al. 2000). N₂O release from stored manure was low when NH₃ was high (Külling et al. 2002). In contrast, Béline et al. (1999) found that concentration of NH₃ does not affect N₂O production when nitrification is dominant.

Methods of Measuring Gaseous Emissions from Stored Manure

Most methods for quantification of gaseous fluxes from stored manure are based on methods developed for measurement of gaseous emissions from soils. These can be broadly classified into chamber or micrometeorological

methods (Lapitan et al. 1999). The location of manure storage tanks in proximity to complex turbulent structures, such as barns and silos, has led to the development of methods specifically suited for measurement of gaseous fluxes from manure stores, as reviewed here.

Chamber Methods

Chamber methods consist of placing an enclosure over a source of interest and capturing the emitted gases in the headspace of the enclosure. Typically source areas are small ($< 1 \text{ m}^2$) (Husted 1993), and effects on local environmental conditions restrict the continuous use of these methods over extended periods of time.

In the case of “closed” or non-steady chambers, the gaseous flux from the source area is proportional to the increase in headspace gas concentration over time. For ventilated chambers (“open” or steady-state), the increase in gas concentration in the out-going air stream, when compared with the incoming air stream, is proportional to the gaseous flux from the source area (Livingston and Hutchinson 1995).

Chamber methods have been used for in situ measurement of CH_4 and N_2O fluxes, as, for example, from windrows of cattle and pig manure (Hellebrand and Kalk 2001), and feedlot cattle manure (Hao et al. 2001). Ease of use, portability, and low cost are often cited as advantages of chamber methods. Enclosed sources, such as manure storage under barns, can be treated as “mega-chambers” where air exchange rates and gaseous concentrations in out-going and in-coming air are monitored. When studying processes influencing gaseous emissions, laboratory experiments under controlled conditions are carried out using sampled manure (Brown et al. 2000; Massé et al. 2003a). The analytical technique most commonly used for measurement of trace gas concentrations with chamber methods is gas chromatography (Lapitan et al. 1999), but use of fast response gas analysers allows for automated, on-site analysis (Thompson et al. 2004).

Micrometeorological Methods

Micrometeorological methods, such as the eddy covariance, flux-gradient, and MMB methods do not interfere with gas exchange processes between the surface source and the atmosphere, and are ideally suited for continuous flux measurements (Denmead 1995). Assumptions regarding airflow limit the eddy covariance and flux-gradient methods to situations with large fetches. Anaerobic lagoons approach this condition and have been monitored using the flux-gradient method (Sharpe and Harper 1999), but surrounding inhomogeneities can present violations to basic assumptions in these methods (Wilson et al. 2001). On the other hand, the MMB is appropriate for flux measurements from small emitting areas such as manure storage tanks (Wilson et al. 2001).

The MMB method, first deployed for measuring NH_3 flux from small fields that had received an application of nitrogen fertilizer (Denmead et al. 1977), is also termed the Integrated Horizontal Flux (IHF) method (Wilson and Shum 1992), since the gas flux emitted is given by the difference

in horizontal flux integrated over height between upwind and downwind positions in relation to the source area. For CH_4 and N_2O , trace gases with high background concentration, upwind concentration measurements are needed. For CH_4 emissions from landfills and from ranging sheep, line samplers were placed at four heights and the MMB method was applied in rectangular plots (Denmead et al. 1998; Leuning et al. 1999). In a similar setup (Harper et al. 1999), the resolution needed to resolve CH_4 concentration differences ($< 0.1 \text{ ppmv}$) was found to be close to the limits for non-dispersive infra-red analyzers, but well within specifications of tunable diode laser (TDL) analyzers (Wagner-Riddle et al. 2005). Recent advances in TDL spectroscopy (Edwards et al. 2003) have enabled CH_4 and N_2O concentration measurements with the time response, sensitivity and noise level needed for the MMB method.

Indirect Methods

In contrast to direct measurements using the approaches described above, atmospheric dispersion models allow for indirect deduction of emission rates. An approximate solution to the advection-diffusion equation was used to back-calculate tracer gas (SF_6 and CH_4) releases using downwind concentration measurements at several heights and positions (Kaharabata et al. 2000). Others inferred the emission rate from an artificial CH_4 source from a downwind open-path laser concentration measurement using a backward Lagrangian Stochastic (bLS) model (Flesch et al. 2004). In the latter study, the ratio of predicted and actual release rate was 1.02 with an acceptable variability of 0.2 after some selected and biased periods were excluded. The application of the bLS technique to determine emissions from stored manure is promising but additional comparisons are needed to determine its applicability in field conditions. For example, the same authors (Flesch et al. 2004) state that the distance from the source should be such that the increase in concentration above background is accurately measured. Open-path lasers have the advantage of providing line-average concentration measurements, but pressure-broadening effects decrease their sensitivity, due to broader absorption line widths that accompany the increase in collisional broadening of the line (Wagner-Riddle et al. 2005). The lowest release rate used in the bLS study (Flesch et al. 2004) was above the range in mean CH_4 fluxes measured from stored liquid swine manure using the MMB method (Wagner-Riddle et al. 2006) ($4700 \text{ vs. } 20 \text{ to } 1000 \mu\text{g m}^{-2} \text{ s}^{-1}$). Alternatively, concentration measurements could be carried out at several points downwind of sources using a 16-intake sampling system and TDL analyzers (Wagner-Riddle et al. 2006). This may allow for application of the bLS method to determine emission from weaker sources as previously evaluated.

Comparison of Measurement Techniques

A comprehensive comparison of measurement techniques is beyond the scope of this review. Briefly, there are several advantages and disadvantages associated with each method discussed above. Vented closed chambers are easily constructed and deployed in the field, with gas analysis per-

formed in the laboratory using gas chromatographs. They can be used in small plot studies, but measurements are time consuming since four or more samples are needed per chamber for each flux measurement, making it costly and impractical to obtain many measurements in one day. In contrast, micrometeorological methods are ideally suited for long-term studies, but fast-response and low resolution gas analysers are required.

Few studies have been conducted comparing several methods of gas flux measurements, and these have mostly focussed on gas emissions from soils, using chamber and traditional micrometeorological techniques, such as eddy covariance and flux-gradient (Lapitan et al. 1998). In one study, flux-gradient and chamber techniques showed good agreement in hourly data, if the emission footprint was taken into account (Christensen et al. 1996).

Other micrometeorological methods, which are ideally suited for measurement of gas fluxes from manure storage, have not been extensively compared with chamber methods. A recent study addressed some of the concerns related to methodology comparison by using chamber, IHF and bLS methods for measurement of trace gas emissions from composting piles (Sommer et al. 2004a). The bLS method with an NH_3 open-path laser and IHF method with NH_3 passive flux samplers did not agree well in the measured accumulated fluxes (0.33 vs. 0.7 kg $\text{NH}_3\text{-N}$ over 7 d), but assumption of emissions over the first 1.5 h (missed by the bLS method) led the authors to conclude emissions were similar. Comparisons of these methods were not carried out for CH_4 or N_2O due to analytical constraints. Clearly, additional studies with comprehensive comparisons of methodologies are needed to allow comparison of results obtained from studies using contrasting methodologies.

Modelling CH_4 and N_2O Emissions from Manure Storage

Gas emissions from animal manures vary with type of animal, diet, management of manure, and climate conditions (National Research Council 2003). Due to these factors, and the paucity of measurements in Canadian conditions, livestock-related emission estimates of these gases are very uncertain (Janzen et al. 1998). To date, global, national and regional estimates of emissions have been obtained through the "EF" approach, where a typical EF, expressed as mass $\text{animal}^{-1} \text{yr}^{-1}$, is multiplied by animal population numbers for a region (IPCC 2000). Recently, the need for a process-based modelling approach has been identified (NRC 2003).

IPCC Recommended Emission Factors

Current estimates of CH_4 and N_2O emissions in Canada have been obtained using IPCC Tier 1 methodology (Matin et al. 2004). For CH_4 , this method involves multiplying default EF by the population of animals in each livestock category (Table 2). For N_2O , default EF of given manure management systems are multiplied by the nitrogen excretion associated with each waste management system (IPCC 2000).

IPCC has also developed a Tier 2 approach for estimating CH_4 emissions from manure management systems (IPCC

2000). This approach uses country-specific inputs of volatile solids estimated by dry matter intake, feed digestibility and ash content of manure, a CH_4 conversion factor based on climate and type of manure storage, the distribution of manure management systems throughout the country, and the maximum CH_4 potential (B_0) of a manure based on species and diet. Table 2 lists EF for Canada calculated using this approach. The difference in EF listed is largely the result of manure storage used predominantly in Canada for each livestock category (e.g., solid/pasture for beef vs. liquid for dairy cattle), but diet also plays a role in this approach. It is expected that the Tier 2 approach will be used in the Canadian Greenhouse Gas Inventory in the near future.

Dynamic Mechanistic Models

Process-based (dynamic mechanistic) models are required in order to describe accurately and predict GHG emissions from manure storage, as affected by management and climatic conditions. Production of CH_4 and N_2O in stored manure is affected by several factors, as described above, and a comprehensive model should account for these. However, process-based models describing GHG emissions from manure during storage are lacking. Recently, Sommer et al. (2004b) proposed algorithms that link C and N turnover and predictions of CH_4 and N_2O emissions during handling of liquid manure. Testing of proposed algorithms requires year-round data on GHG emission from manure. Laboratory studies on anaerobic digestion (AD) or incubations can help provide increased understanding of processes. However, a database of manure composition and in situ trace gas fluxes from contrasting manure storage systems is required for development and verification of process-based models that reflect typical manure storage. Of particular importance in such a database would be a complete description of animal characteristics, such as age, weight, performance and diet, in order that GHG emissions from manure can be linked to animal production.

Treatment Options for Mitigation of Emissions from Manure

There are several techniques that have been suggested to reduce gas fluxes from manure storage; composting, anaerobic digestion, diet manipulation, covers and solid-liquid separation are discussed here. Results of the Farm Environmental Management Survey show that manure is not commonly treated in Canada, and that when treatment was applied it was to manure from beef cattle, rather than dairy or swine (Statistics Canada 2004).

Compost

Compost can be defined as "an aerobic process of decomposition of organic matter into humus-like substances and minerals by the action of microorganisms with chemical and physical reactions" (Peigné and Girardin 2004). Composting has been shown to decrease odours, pathogens and weed seeds, as well as to increase ease of transport by reducing weight and volume of manure (Peigné and Girardin 2004). In addition, composts are often field-applied

in place of raw manure for soil conditioning and fertilization (Yang et al. 2002). Manure treatment via composting can be active, with forced aeration, or passive, with only natural aeration and turning. The Farm Environmental Management Survey found that 37.8% of farms across Canada used composting, but states this number may be an overestimate, as many of the surveyed farmers may have considered solid manure storage as composting (Statistics Canada 2004). Table 4 summarizes emissions from composting found in Canadian studies.

After active composting of liquid hog manure with wheat straw, one study found GHG emissions were reduced to 30% of those from untreated manure (Thompson et al. 2004). However, contributions to air and water pollution during processing via ammonia volatilization and nitrate leaching may reduce its utility as a fertilizer and thereby its desirability as a mitigation measure (Peigné and Girardin 2004). In addition, studies that quantify all environmentally important gas emissions associated with composting, including after field application, to determine if flux reductions during composting counterbalance potential increases in emissions after application are lacking.

Management applied during the composting processes appears to have an important role in determining GHG emissions. Using a modified vented chamber technique on windrow composting, Hao et al. (2001) found that turning the compost led to higher gas diffusion rates and increased porosity that led to significantly higher N_2O fluxes. Conditions necessary for nitrification from the top layer of the windrow, high NH_4^+ and low NO_3^- concentrations, could be maintained with mixing to redistribute N-compounds, resulting in higher N_2O emissions from nitrification in the aerated windrow. However, NO_3^- levels increased and denitrification became more important than nitrification as the study progressed.

Composting liquid swine manure for a period of 2 wk, Thompson et al. (2004) found overall emissions of CH_4 and N_2O were much higher in the treatment without aeration when compared with liquid manure storage. In contrast, the treatment with forced aeration decreased emissions. However, the authors caution that emissions during curing, that is, after the “active” composting phase of their study, may result in a different assessment of the role of composting in GHG emissions. Increased denitrification in compost over time (Hao et al. 2001) may counteract the decreased CH_4 emissions observed during the aeration phase of the Thompson study.

Treating manure with sulphur compounds such as phosphogypsum led to exponentially diminished CH_4 emissions with increasing sulphur content (Hao et al. 2005). This reduction may be attributed to sulphate toxicity to methanogens, competition between methanogens and sulphur-reducing bacteria, as explained above, or increased levels of NH_4^+ in the compost (Mahimairaja et al. 1994). Phosphogypsum was not shown to affect N_2O , but N_2O losses did increase with acidity (Hao et al. 2005). Other studies have found sulphur additions to reduce N losses during composting by decreasing the pH of compost without decreasing the level of decomposition (Mahimairaja et al. 1994).

Bedding additives in manure also affect the flux of gases from compost. In a 99-d study, Hao et al. (2004) found that both CH_4 and N_2O were higher from straw-bedded manure than from wood-chip bedded manure, with results significant only for N_2O production during the last 50 d. Regardless of amendment, emissions were highest at the beginning of the trial. Denitrification was assumed to be the primary process involved in N_2O formation due to a high correlation between NO_3^- and N_2O . Extreme anaerobic conditions led to unstable N_2O quickly being reduced to N_2 . In contrast, Mahimairaja et al. (1995) found that C-rich amendments like straw or wood-chips reduced the loss of N_2O by denitrification. Studies outside Canada have shown that density of the compost affects emissions, with lower density (higher porosity) resulting in lower emissions (Sommer and Moller 2000). A Danish study of deep-litter compost found very little emission of N_2O and CH_4 during the months of September to April. In compost periods ranging from 50 to 70 d, Hellebrand and Kalk (2001) found CH_4 from dung windrows were highest during the first 3 wk, whereas N_2O was highest in the middle of the composting period.

Anaerobic Digestion

“Anaerobic digestion is a natural process whereby bacteria existing in oxygen-free environments decompose organic matter” (Safley and Westerman 1992), resulting in a biogas of CH_4 and CO_2 and a sludge that is stable and nearly odourless. Anaerobic digesters, built to facilitate decomposition, can function at mesophilic and thermophilic temperatures, but Canadian conditions are most conducive to psychrophilic conditions ($< 20^\circ C$) (Abou Nohra et al. 2003), on which there are few studies. Some mesophilic digesters ($20\text{--}45^\circ C$) have been implemented in Canada, and have adapted to cold climate conditions by using insulated walls or below-ground construction to reduce heat loss and a heat-exchange system, which draws on the heat produced during digestion to regulate digester temperature (National Resource Canada 1999). A digester operating in Iron Creek, Alberta, used approximately 2% of the heat generated during digestion to maintain the digester at a constant mesophilic temperature (West 2004).

Studying low temperature AD, Safley and Westerman (1994) found a linear relationship between CH_4 yield and temperature within the digester. Similarly, Canadian studies have shown that higher temperature lead to greater CH_4 production (Ghaly 1996) and that low temperatures on Canadian farms during late fall through to early spring may result in low CH_4 production (Massé et al. 2003a). Massé et al. (2003b) found that fluctuating temperatures temporarily lowered CH_4 production from digestion of swine manure, and that after a drop in temperature followed by a return to the original temperature, CH_4 production was slow in returning to original levels. In a review on psychrophilic AD, Kashyap et al. (2003) noted that bacteria working at low temperature are acclimatized mesophiles rather than true psychrophiles. In addition, organic acids accumulating while manure temperatures are low and causing a decrease in manure pH may inhibit methanogenic bacteria even when

Table 4. Emissions of CH₄ and N₂O from composted manure in selected Canadian studies

Type of compost	Manure	Date	CH ₄ (kg C m ⁻² d ⁻¹)	N ₂ O (g N m ⁻² d ⁻¹)	Reference
Passive active	Beef feedlot	1997 May–Aug. (99 d)	0–0.04 0–0.02	0–0.60 0–0.92	Hao et al. (2001)
Active w/ straw-bedded manure Active w/ wood-chip bedded manure	Beef feedlot	2000 Jul. 12–19 Oct.	1.254 1.141	0.0109 0.0107	Hao et al. (2004)
Active passive [in-vessel (13 d) + curing (11 d) stages]	Liquid swine	2000 Sep.–Oct.	0.1004 0.186	0.704 1.24	Thompson et al. (2004)

temperatures return to normal (Miner et al. 2000). By regulating temperature via insulation and recycling of heat, the slump in CH₄ production resulting from high concentrations of organic acids and from bacteria re-acclimating to temperature could be avoided.

Other factors causing an increase in CH₄ production from AD are longer storage periods, low TS content (when measured on a per kilogram of volatile solids basis), and species, with swine slurry able to produce more CH₄ than cattle slurry (Massé et al. 2003a). As with stored manure, high concentrations of NH₄⁺, VFAs and sulphur compounds can be toxic to methanogens (Massé et al. 2003a; Oremland and Polcin 1982) and may therefore be limiting factors for AD.

Inocula are used in psychrophilic conditions to reduce start-up time. When testing the efficacy of different inocula on a substrate of swine manure, Abou Nohra et al. (2003) found that, of those tested, cattle manure proved to be the best inoculum due to its high soluble chemical oxygen demand. The length of time before methanogenesis began did not affect the total CH₄ produced over the 100-d study. A European study examining low temperature AD of cattle and pig manures found that start-up of digestion below 15°C requires inoculation, and that using an inoculum already acclimatized to low temperatures will increase CH₄ yields (Zeeman et al. 1988).

Methane produced by digesters can be captured and burned as fuel, hence increasing methanogenesis is desirable in AD systems, as the increased CH₄ production from AD results in decreased CO₂ emissions from fossil fuel combustion. Currently, it is estimated that less than 1% of manure in Canada is anaerobically digested (Marinier et al. 2004), but several projects are underway to investigate the feasibility of both low and medium temperature digestion, which may qualify for carbon credits (West 2004). While the mitigation potential of GHG emissions through AD is obvious, the evaluation of carbon credits generated is associated with the GHG emissions from stored manure avoided through AD treatment. Thus, lower GHG emissions associated with low temperature of stored manure in ambient conditions in Canada also has an effect on this evaluation. In addition, GHG emissions after AD treatment, including during storage and application of treated manure to soils, need to be considered.

Diet

The Farm Environmental Management Survey found that 3.8% of farms, predominantly swine farms, use additives or feeding strategies to reduce nutrient content in manure (Statistics Canada 2004). Very little is known about the effects of diet on emissions from stored manure. In the case of ruminants, research has focussed on reduction of CH₄ emission due to enteric fermentation as discussed above. Most studies on swine diet manipulation have tried to reduce odours or N content and NH₃ emission. In a review of the effects of diet manipulation on odour and GHG reduction from swine, Clark et al. (2006) have suggested that while most research has focussed on nutrient efficiency and digestion, these factors are in fact related to GHG reduction.

One study supplemented a swine diet with 5% chicory inulin and found that the rate of NH₃ emission increased, as did the total faecal nitrogen content (Rideout et al. 2004). Total amount of N in the urine is also related to the amount of dietary N-intake (Mosier et al. 1998). Hence, as N₂O emissions are related to the amount of N in the manure, they should potentially be reduced with lower N excretion. Examining the effect of dietary protein and non-starch polysaccharide on emissions from swine manure, Clark et al. (2005) found no effect of the latter, except in combination with low protein treatments. Velthof et al. (2005) found that increasing non-starch polysaccharide corresponded to increasing CH₄. CO₂ and CH₄ were affected by protein content, with higher emissions resulting from lower protein treatments (Clark et al. 2005), corroborating similar findings with dairy cattle by Külling et al. (2001). The lower pH and sulphur content reported in the low protein diet (Clark et al. 2005) may have diminished the competitive effects of sulphate-reducing bacteria. In contrast, a Dutch study showed that CH₄ decreased with low protein due to decreasing VFAs (Velthof et al. 2005). Further research is required to understand the factors at play behind these contrasting results.

For N₂O, while Clark et al. (2005) showed only negligible emissions from liquid swine manure, a Swiss study found N₂O from liquid dairy cattle manure to increase with protein content, though the overall GHG emissions considering CH₄ remained lowest at high dietary protein (Külling et al. 2001). Dietary protein has been shown to relate positively to urinary N excretion (Canh et al. 1998), suggesting

that N_2O emissions at high protein levels relate to increased diet digestibility and N availability.

Studying anaerobic digestion of feedlot manure, Hashimoto et al. (1981) argued that CH_4 yield increased as more grain was incorporated into the diet. In contrast, Boadi et al. (2004b) found that varying forage-to-grain ratio alone did not affect N_2O and CH_4 emissions from feedlot manure. Similarly, a 5–7 wk study of dairy cattle found no significant difference between forage types in emissions of N_2O and CH_4 from manure (Külling et al. 2003). Emissions may therefore be related largely to dietary N content (Boadi et al. 2004b) and storage conditions, though other studies have found dry matter, total C and VFAs to affect GHG production as well (Velthof et al. 2005).

Covers

To our knowledge, no published Canadian studies have looked at how covering manure storage would affect gas losses. In Europe, covers have been built in an attempt to reduce odour or capture biogas. This is done by trapping the gas so that it cannot escape, and by preventing wind from removing the gas and increasing the vapour pressure difference that would bring more gas to diffuse from lower depths in the manure tank toward the surface (Miner et al. 2000). Captured biogas can be burned off or used as a fuel, and reduce net GHG emissions as CH_4 is oxidized to CO_2 , whose global warming potential is 21 times lower than that of CH_4 . Solid materials in slurries will float to the top and form a natural surface crust, but straw or other materials can be added to make a floating cover, or impermeable covers made of rubber or synthetic materials can be installed. Emissions of CH_4 are higher from slurries that had not formed their own crust than from those that had, but the effectiveness of the natural crust decreased as increasing manure temperature caused the crust to dry and become porous (Husted 1994). Straw crusts were found to be most effective at decreasing CH_4 (Sommer et al. 2000). In contrast, when comparing natural crusts, straw and leca pebbles (burnt montmorillonitic clay), Sommer et al. (2000) found that only covered slurries were producing N_2O , and then only when evaporation was greater than precipitation, causing covers to dry and create aerobic conditions at the surface. Leca pebbles were found to allow fewer emissions than straw. Temperature was not found to affect the production of N_2O from covered slurries (Sommer et al. 2000).

Solid-liquid Separation

The agricultural practice of solid-liquid separation of manure has been used in part to increase the ease of handling and transporting effluent and to reduce odour, but may also be used as a tactic to reduce GHG. Separated solids can be used in conjunction with anaerobic digestion for biogas production (Holmberg et al. 1983). Using only the solid portion of the manure for anaerobic digestion can increase the volatile solids concentration of the substrate and allow for greater CH_4 yield than from the whole manure (Moller et al. 2004). The more complete the transfer of volatile solids from the liquid to the solid portion of the manure, the more

CH_4 can be produced. This technique is expensive and little research has been done to determine its practicality and economic efficiency for Canadian conditions.

NITROUS OXIDE AND METHANE FROM FIELDS

Pasture, where manure is left untreated, is often used for dairy cattle, beef cattle, and sheep, especially in summer, but detailed estimates of the proportion of manure excreted at pasture in Canada are lacking. Consultation with a small group of experts throughout Canada yielded rough estimates of 50, 20 and 60% of manure excreted at pasture for beef cattle, dairy cattle and sheep, respectively (Marinier et al. 2004). In addition, 300 Mt of manure are applied each year to Canadian croplands, including managed grasslands (Coote and Gregorich 2000).

Minor levels of CH_4 have been found to be emitted from manure deposited at pasture (Sherlock et al. 2002). Despite the expected increase in methanogenic potential of soil with addition of large amounts of water, Jarvis et al. (1995) did not find an effect of urine on CH_4 emission during grazing. Yamulki et al. (1999) measured CH_4 emission from soils and also found the majority of CH_4 from excreta came from dung. The authors reported that there were large variations in CH_4 emission from excreta that are attributed to climatic differences at the time of deposition of dung. They estimated that on average, 0.96 and 0.03 g CH_4 d⁻¹ cow⁻¹ is emitted from dung and urine, respectively in grazing cattle. These emission estimates from excreta in grazing animals are less than 1% of enteric fermentation, and much smaller than the emission from manure managed predominantly in liquid form (e.g., dairy and swine, Table 2).

On the other hand, dung and urine deposited at pasture, and manure applied to cropped fields, including grasslands, have been shown to be important sources of N_2O (Janzen et al. 1998). In the Canadian GHG inventory based on IPCC (2000), these emissions are listed under “soils”, and amount to approximately 6 Mt and 4 Mt CO_2 -equivalent, respectively (Chang Liang, Environment Canada, personal communication), or approximately 17% of Canadian agricultural emissions. These estimates were obtained assuming manure N deposited at pasture contributes 0.02 kg N_2O -N kg⁻¹ N excreted by the animal, and manure N applied to soils 0.0125 kg N_2O -N kg⁻¹ N applied. This latter EF is the same value used for inorganic N addition to soils. But many studies have suggested EF for manure N could be higher than for inorganic N. In a recent comparison of several Canadian data sets, Helgason et al. (2005) confirmed the necessity of separate EF for manured and non-manured soils. Gregorich et al. (2005) observed higher N_2O emissions resulting from liquid manure or mineral fertilizer (~2.8 kg N_2O -N ha⁻¹ yr⁻¹) when compared with solid manure (0.99 kg N_2O -N ha⁻¹ yr⁻¹).

The factors controlling N_2O production in soils and potential mitigation practices related to inorganic and organic N amendments have been extensively reviewed (Davidson 1991; Granli and Bockman 1994; Grant et al. 2004; Saggar et al. 2004b). Measurement of N_2O emissions from soils has also been the subject of considerable attention (Lapitan et al. 1999; Denmead et al. 2000). Process-based

models that include detailed algorithms for water, energy, C and N cycles in crop and grasslands have been developed, such as DNDC (Li et al. 1992a, b), and DAYCENT (Parton et al. 1998; Del Grosso et al. 2001).

In grazed lands the C and N dynamics are affected by the presence of animals with consequences for the biochemistry of gaseous N emissions as reviewed by Bolan et al. (2004). Hence, models require changes to describe the N input to soils via animal excretion (Saggar et al. 2004a). Ideally, modelling soil N₂O emissions should be linked to nutrient flows through animal and manure component as depicted in Fig. 1.

INTEGRATED STUDIES

There is a lack of studies investigating GHG emissions from livestock, through manure storage and following manure excretion at pasture or field application of manure, particularly studies that evaluate how changes in one component may affect emissions in the other components shown in Fig. 1. Dietary manipulation for reduced CH₄ production in ruminants may alter manure composition such that CH₄ and/or N₂O emissions from manure and soils are affected. Likewise, manure treatments can change manure characteristics and N₂O emission from soils after manure application.

A Swiss study by Külling et al. (2002) considered the effects of two different dietary supplements, lauric acid (C12) and stearic acid (C18), on emissions of CH₄ from enteric fermentation, and N₂O and CH₄ from two manure storage systems. Cows fed the C12 diet refused approximately half of the concentrate and thus produced less ruminal CH₄ overall, but equal amounts of CH₄ on the basis of per unit of fibre digested. After 14 wk of storage, manure from the C12 diet produced more CH₄ than the C18 manure. N₂O emissions were not affected by diet, except in the solid farmyard manure where C18 produced more than twice the N₂O of C12.

An Austrian study examined CH₄ emissions from dairy cattle in a tie-stall barn and N₂O and CH₄ from two storage systems (Amon et al. 2001). They used a mobile open-dynamic-chamber covering 27 m², which they could move between the animal houses and storage areas. Inside the barns, neither N₂O nor CH₄ varied with manure management system. Methane emissions peaked in the morning and afternoon after feeding the cows. Overall gas losses from storage were lower from composted manure than from anaerobically stacked manure, but the effect of these treatments on emissions after spreading was not quantified.

Boadi et al. (2004b) found that CH₄ production from steers fed a low forage-to-grain ratio was 42% higher than when fed a high forage:grain ratio diet supplemented with sunflower seed, but diet had no effect on CH₄ and N₂O from the manure pack. They attributed this effect to dilution of faecal and urinary excretions through straw bedding, masking the effect of diet. Reducing the substrate for microbial action, as when N content of animal excreta is reduced, is expected to reduce the amount of N₂O emitted from soils. A simulation study by Kebreab et al. (2000) showed that increasing energy concentration of the diet using low degradable starch sources such as corn in concentrates could

reduce not only the total amount of N in excreta but also the proportion of N in urine, which in turn could reduce ammonia and N₂O emissions. Indeed, Velthof et al. (2005) showed that potential N₂O emissions from soil, as evaluated in a laboratory study, were decreased by decreasing the crude protein content of swine diets. In addition, potential ammonia and CH₄ emissions from anaerobically stored manure were decreased when protein content in diets was decreased.

Studies that integrate GHG emissions from all components associated with animal production are needed in order to evaluate mitigation options thoroughly. Such studies will require a combination of field and laboratory experimentation, as well as mathematical modelling. Schils et al. (2005) used a modelling approach at the farm-level to evaluate potential options for mitigation of GHG emissions from ruminant livestock systems. Their model used IPCC (1997) EF and considered C and N flows between animal, manure, soil, crop and feed pools. Ideally, such an approach could be improved upon by gradually implementing process-based models to describe emissions from each pool.

CONCLUSIONS

Knowledge of the processes and mitigation options surrounding CH₄ and N₂O from enteric and manure fermentations has increased in recent years, but gaps still exist. This review has identified some potential areas for further research.

Further work focussing on the entire cycle of GHG formation from feed formulation, animal metabolism, excreta treatment and storage, to field application of manure needs to be conducted. The holistic nature of this approach would allow identification of areas where mitigation of one gas (e.g., CH₄) results in increasing emission of another (e.g., N₂O). In addition, potential effects of dietary additives to manure treatment, storage, and field emissions could be assessed. Increased knowledge of microflora and the processes of methanogenesis both in the rumen and manure would help investigating mitigation options. Cost benefit analysis of management systems and diet selection should also be studied in order to ascertain the practicality and ease of implementation of mitigation measures at the producer level.

Several studies on emissions from manure have been conducted for a short period of time and extrapolated to obtain an annual estimate. Year-round measurement would be more accurate and may provide further information on the effect of climate and weather conditions on emissions from manure storage and field.

The results from experiments on GHG across Canada and the rest of the world are variable. In particular, effects observed with *in vitro* experiments are not replicated *in vivo* possibly due to loss of a controlled environment, sensitivity or longer time frame (with probable microbial adaptation) in the rumen. There are also scaling issues, which need to be addressed where experiments with individual animals are used to predict emissions from a group of animals and vice-versa. Measurement techniques used are also variable and standardization and documentation of supporting variables such as detailed feed characteristics might help solve some

of the discrepancies observed. A database containing such supporting variables, observed GHG emissions and measurement techniques needs to be compiled to give added value to those experiments conducted though development of both statistical and process-based, mechanistic models.

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