# Gaseous Nitrogen and Odour Emissions Following Manure Application Under Grassland and Cultivated Systems

by

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#### **Dedication**

This thesis is dedicated to my wife Nkosazana, my daughter Nomalanga my parents (Moses Mjibha Mkhabela and my late mother Sellinah Mlahlu Mkhabela (La-Mahlalela)), my foster mother Grace E. Retson and my friend Jabulani Mamba, who died a month after I started my Ph.D. programme.

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### List of Abbreviations and Symbols

DCD: Dicyandiamide

S: Slurry

NI: Nitrification Inhibitor

NH<sub>3</sub>: Ammonia

NH<sub>4</sub><sup>+</sup>-N: Ammonium-Nitrogen

NO<sub>3</sub>-N: Nitrate-Nitrogen

N<sub>2</sub>O: Nitrous Oxide

F<sub>NH3</sub>: Ammonia Flux

F<sub>N2O</sub>: Nitrous Oxide Flux

NT: No-Tillage

CT: Conventional Tillage

WFPS: Water-Filled Pore Space

ANOVA: Analysis of Variance

DMRT: Duncan Multiple Range test

R<sup>2</sup>: Coefficient of Determination

IPCC: Intergovernmental Panel on Climate Change

<sup>o</sup>C: Degrees Celsius

FAO: Food Agriculture Organisation

GC: Gas Chromatograph

GHG: Greenhouse Gas

H<sub>3</sub>BO<sub>3</sub>: Boric Acid

H<sub>3</sub>PO<sub>4</sub>: Phosphoric Acid

VPD: Vapour Pressure Deficit

DM: Dry Matter

TAN: Total Ammoniacal Nitrogen

BREB: Bowen Ratio Energy Balance system

TDR: Time Domain Reflectometry

 $\theta_v$ : Volumetric Soil Water Content

ET: Evapotranspiration

PVC: Polyvinyl Chloride

BEEC: Bio-environmental Engineering Centre

SR: Streets Ridge

DAP: Diammonium Phosphate

TPS: Theoretical Profile Shape

OC: Odour Concentration

OU: Odour Unit

ha: Hectare

T: Metric Tonne

Mg: Mega gram

d: Day

h: Hour

min: Minute

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#### **Abstract**

Livestock manure is a valuable source of plant nutrients, however, if poorly managed it can have negative environmental impacts. The major environmental impacts and health concerns associated with manure are the loss of nitrogen (N) in the form of nitrate (NO<sub>3</sub>), ammonia  $(NH_3)$  and nitrous oxide  $(N_2O)$ , as well as odour emissions. Laboratory and field experiments were conducted in Truro and Great Village, Nova Scotia to evaluate the effect of several management strategies on NH<sub>3</sub>, N<sub>2</sub>O and odour emissions. The strategies evaluated include; (i) use of a nitrification inhibitor (dicyandiamide), (ii) soil liming, (iii) slurry application rate, (iv) soil water status, (v) slurry dilution, and (vi) simulated rainfall soon after slurry application. The study also evaluated the effects of meteorological conditions on NH<sub>3</sub>, N<sub>2</sub>O and odour emissions, for the purpose of identifying the most appropriate conditions under which manure can be applied with minimum emissions. Results showed that dicyandiamide had no effect on either NH<sub>3</sub> or N<sub>2</sub>O emissions. Liming soil to a pH ≥6.3 decreased N<sub>2</sub>O, but increased NH<sub>3</sub> emissions. Generally, N<sub>2</sub>O emissions from the field experiments were low (~5 g N ha<sup>-1</sup> d<sup>-1</sup>) even with high (180 t ha<sup>-1</sup>) slurry application rates. This was due to low soil NO<sub>3</sub>-N (<5 mg kg<sup>-1</sup> soil) contents caused by slow nitrification activity on these acidic soils. Additionally, estimated indirect N<sub>2</sub>O emissions (i.e., emissions due to volatilised NH<sub>3</sub>) were higher than direct emissions. Increasing slurry application rate increased NH<sub>3</sub> losses and to a lesser extent odour emissions, but had no effect on N<sub>2</sub>O emissions. Applying slurry to wet soils increased NH<sub>3</sub> losses by 8% compared to dry soil, but had no effects on N<sub>2</sub>O and odour emissions. Slurry dilution and simulated rainfall reduced NH<sub>3</sub> losses on average by 41 and 45%, respectively, but had no effect on N<sub>2</sub>O emissions. With regard to odour, dilution reduced odour emissions on average by 27%, while simulated rainfall increased odour emissions by 15%. Ammonia losses increased with higher air and soil temperature, net radiation, evapotranspiration and vapour pressure deficit, while N<sub>2</sub>O emissions were not affected by the recorded meteorological variables. Meanwhile, odour emissions increased with higher windspeed, net radiation and evapotranspiration. Both NH<sub>3</sub> and odour emissions can therefore, be reduced by applying slurry during cool and calm conditions, however, such conditions may increase odour persistence. The fact that estimated indirect N<sub>2</sub>O emissions were higher than direct emissions suggests that more effort should be directed towards reducing NH<sub>3</sub> losses following application of slurry on these acidic soils.

In addition, field experiments were performed from 2003 to 2005 at Streets Ridge (SR), Cumberland County, Nova Scotia and Bio-Environmental Engineering Centre (BEEC), Truro, Nova Scotia to evaluate the impact of tillage on NH<sub>3</sub>, N<sub>2</sub>O, denitrification rates, ratios of denitrification end-products (N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub>), and soil and drainage water NO<sub>3</sub>-N concentrations following surface application of beef and dairy manure. Over the two seasons, manure incorporation in the conventional tillage (CT) reduced NH<sub>3</sub> loss on average by 86% at SR and 78% at BEEC relative to no-tillage (NT). At both sites and both seasons, denitrification rates and N<sub>2</sub>O emissions in NT were generally higher than in CT. Conversely, N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratios were lower in NT, indicating more complete reduction of N<sub>2</sub>O to N<sub>2</sub>. Similarly, soil and drainage water NO<sub>3</sub>-N concentrations were generally lower in NT. Thus, NT can be used to reduce NO<sub>3</sub>-N leaching to groundwater, albeit with trade-offs.

#### CHAPTER 1

#### 1.0 INTRODUCTION

#### 1.1 Problem Statement

Confined intensive livestock production systems generate high volumes of manure. In 1996, Canadian livestock produced an estimated 132 million tonnes of manure, most of which was subsequently applied to agricultural fields (Gregorich et al., 2005; Statistics Canada, 2001). Livestock manure is a valuable source of plant nutrients; however, if poorly managed it can result in serious environmental problems such as water and air pollution (Rotz, 2004).

The major environmental concerns associated with livestock manure are the loss of nitrogen (N) through ammonia (NH<sub>3</sub>) volatilisation, nitrous oxide (N<sub>2</sub>O) emission and nitrate (NO<sub>3</sub><sup>-</sup>) leaching, and the generation of malodours (FAO, 2001). Ammonia is an important atmospheric pollutant with a wide variety of impacts including acidification and eutrophication of N-deficient ecosystems (FAO, 2001) and N<sub>2</sub>O formation (Ferm, 1998). The Intergovernmental Panel on Climate Change (IPCC, 1996b), estimates that for every 1 kg of NH<sub>3</sub>-N volatilised, 0.01 kg of N<sub>2</sub>O-N is formed. Ammonia loss is mainly governed by the difference in the NH<sub>3</sub> partial pressure between the atmosphere and the manured surface. Factors that regulate NH<sub>3</sub> volatilisation from field-applied manure include meteorological conditions, soil and manure characteristics, and management practices during and after manure application (FAO, 2001; Gordon et al., 2001; Rotz, 2004).

Nitrous oxide is a greenhouse gas (GHG) that contributes to global warming and the depletion of the ozone layer (Crutzen, 1981; IPCC, 1996b). Greenhouse gases partially

absorb outgoing infrared radiation, resulting in increased mean global surface temperature. Records show that the mean global temperature has risen by about  $0.6^{\circ}$  C since the  $19^{th}$  century, partly due to GHG's (IPCC, 1996b). Nitrous oxide is produced in soils through nitrification and denitrification processes. Its production is mainly influenced by N availability, carbon (C) supply, soil moisture content, soil temperature and rainfall (Dobbie and Smith, 2003; Granli and Bøckman, 1994), and freezing and thawing (Burton and Beauchamp, 1994). Agricultural management practices such as inorganic fertiliser N and manure application, crop residue management, and tillage also impact  $N_2O$  emissions (Gregorich et al., 2005).

High NO<sub>3</sub> leaching losses are associated with high fertiliser N and manure application rates and excessive soil moisture conditions (Varshney et al., 1993; Yadav, 1997). Elevated levels of NO<sub>3</sub> in the soil profile constitute a major health risk to both livestock and humans who depend on groundwater aquifers for supply of drinking water. Nitrate is converted to nitrite (NO<sub>2</sub>) in the digestive system of infants, which inturn reacts with haemoglobin causing a condition called methemoglobinaemia or blue-baby syndrome, which can be fatal in some cases (Comly, 1945). Nitrate is also a precursor for N<sub>2</sub>O production through denitrification (Granli and Bøckman, 1994).

Odours are without doubt the dominant nuisance issue affecting livestock producers, with the potential to reach beyond the production site. Storage and field spreading of manure generates strong odours, which create conflicts between producers and neighbours. Some components of odours have negative impacts on plants, livestock and humans (AAFC, 1998b; Hobbs et al., 1999). Therefore, sustainable agricultural production has to combine low N

losses with acceptable odour emissions.

Management strategies used to reduce NH<sub>3</sub> and odour emissions from field-applied manure include injection, incorporation of manure or irrigation soon after spreading, diluting or acidifying manure before spreading, and using proper application rates (Malgeryd, 1998; Rotz, 2004). There is however, a growing concern that some management strategies employed to abate emissions of one gas may increase emissions of the other (FAO, 2001; Ferm et al. 1999; Flessa and Beese, 2000; IPCC, 1996b; Sherlock et al., 2002; Weslien et al., 1998; Wulf et al., 2002), creating a tradeoff between these gases. For example, Wulf et al. (2002a,b) found that some application techniques such as incorporation, injection and trail shoe, which are used to reduce NH<sub>3</sub> emissions, may significantly increase N<sub>2</sub>O emissions. They recommended that NH<sub>3</sub> measurements, should be included in experiments designed to evaluate GHG emissions. Flessa and Beese (2000) and Skiba et al. (2002) reported that direct drilling of manure enhanced N<sub>2</sub>O emissions due to poor aeration. Similarly, Ferm et al. (1999) when studying NH<sub>3</sub> and N<sub>2</sub>O emissions from field-applied pig slurry, found that broadcasting plus harrowing reduced NH<sub>3</sub> losses but increased N<sub>2</sub>O emissions. Malgeryd (1998), reported that irrigation (30 mm) soon after slurry application reduced NH<sub>3</sub> losses by 70%; however, N<sub>2</sub>O and odour emissions were not measured. Since losses of these N compounds may in some cases happen at the same time, it is important that these potential pollutants be evaluated and quantified simultaneously in the same system under study.

Although numerous studies have been conducted to quantify NH<sub>3</sub>, N<sub>2</sub>O and NO<sub>3</sub> losses and to a lesser extent odour emissions following field-spreading of livestock manures, these studies were mostly conducted separately. Moreover, most of these studies were

conducted outside the weather and soil conditions (high annual precipitation and slowly permeable acidic soils) that exist in Atlantic Canada. In order to identify and or develop simple practical farm-level manure management practices that minimise environmental concerns associated with manure spreading, there is a need to study N losses simultaneously in the same system under study.

#### 1.2 Objectives

The overall goal of this research was to simultaneously quantify gaseous N losses and odour emissions following the application of livestock manure (hog and cattle) on both grassland and cultivated systems, and identify farm management practices which reduce environmental impacts associated with manure spreading.

The specific objectives of the study were to:

- (1) assess the impact of several management practices on NH<sub>3</sub>, N<sub>2</sub>O and odour emissions following surface application of hog slurry. Management practices evaluated include:
   (i) use of a nitrification inhibitor (dicyandiamide), (ii) soil liming, (iii) manure application rate, (iv) soil water status at the time of application, (v) manure dilution with water, and (vi) simulated rainfall soon after manure spreading,
- investigate the effect of meteorological conditions (air and soil temperature, vapour pressure deficit (VPD), solar radiation, evapotranspiration) and soil chemical properties (pH, NO<sub>3</sub>-N and NH<sub>4</sub><sup>+</sup>-N) on NH<sub>3</sub> N<sub>2</sub>O and odour emissions,
- (3) quantify N losses in the form of NH<sub>3</sub>, N<sub>2</sub>O and NO<sub>3</sub> as impacted by tillage system following application of cattle manure, and

(4) evaluate the impact of tillage systems on denitrification and the mole fraction of  $N_2O$  ( $N_2O:N_2O+N_2$  ratios) following application of cattle manure.

#### 1.3 Hypotheses

The following hypotheses were postulated for this study:

- (i) Increasing manure rates will result in higher NH3, N2O and odour emissions,
- (ii) When applied at a consistent N rate, manure dilution with water will lower NH<sub>3</sub> and odour emissions but increase N<sub>2</sub>O emissions,
- (iii) Plots with high initial soil water content will emit higher levels of NH<sub>3</sub> and N<sub>2</sub>O, and
- (iv) Nitrification inhibitors will reduce N<sub>2</sub>O losses but will increase NH<sub>3</sub> emissions.
- (v) No-till (NT) will result in higher  $NH_3$  volatilisation, higher denitrification rates and higher  $N_2O$  emissions but lower  $NO_3^-$  leaching than conventional tillage (CT), and (vi) NT will result in lower  $N_2O:N_2O+N_2$  ratios than CT.

#### **CHAPTER 2**

#### 2.0 LITERATURE REVIEW

#### 2.1 Importance of Nitrogen

Nitrogen (N) is one of the most important nutrients required by plants for growth and development, yet it is the most difficult to manage. The supply of N often limits yields of crops. With the increasing demand for food and other agricultural products, producers often apply a large amount of N in the form of mineral and/or organic fertilisers in an attempt to increase yields. The global use of fertiliser N excluding animal manure is at present estimated at 78 million metric T y<sup>-1</sup> and is increasing, particularly in developing countries (FAO, 2001). While the use of N fertiliser can boost crop yields, studies have shown that most crops are very inefficient in the uptake and utilisation of N fertiliser (Beauchamp, 1997; FAO, 2001). It is estimated that plants utilise only about 50 % of the N applied and the rest is lost from the agricultural system as ammonia (NH<sub>3</sub>), nitrous oxide (N<sub>2</sub>O), nitric oxides (NO<sub>x</sub>), di-nitrogen (N<sub>2</sub>) and nitrate (NO<sub>3</sub><sup>-1</sup>) (Beauchamp, 1997; FAO, 2001). These losses have raised concerns about environmental impacts (water, soil and air pollution) and thus producers are under pressure to minimise N losses by adopting N management strategies that are environmentally sustainable.

#### 2.2 Ammonia Volatilisation

Ammonia volatilisation has long been recognised as the major pathway of N loss from organic and inorganic N sources (O'Halloran, 1993). Gordon et al. (2001) found that up to 66% of total NH<sub>3</sub> loss occurred within 10 hours following field-application of dairy manure.

Moal et al., (1995) reported that on average 75% of total NH<sub>3</sub> losses occurred within 15 hours after cattle and pig slurry application. Large losses of NH<sub>3</sub> through volatilisation reduce N availability for plant uptake, and contribute to environmental degradation of natural ecosystems and atmospheric air pollution (Moal et al., 1995; Ryden at al., 1987; Sharpe and Harper, 2002). Ammonia (NH<sub>3</sub>) is the primary neutralising agent for acid gases in the atmosphere and is a common component of atmospheric aerosols (FAO, 2001). Moreover, NH<sub>3</sub> can be oxidised and transformed into N<sub>2</sub>O and this constitutes about 5% of the global N<sub>2</sub>O emissions (Ferm, 1998). The fraction of NH<sub>3</sub> that is converted to N<sub>2</sub>O depends on the type of ecosystem where it is deposited (Weslien et al., 1998). According to Mosier et al. (1996), ammonia volatilisation from agricultural systems is globally important, but its influence on N<sub>2</sub>O emissions has not been directly quantified. In addition, NH<sub>3</sub> is also known to be one of the principal constituents of odour (Zhou and Zhang, 2003).

Factors that influence NH<sub>3</sub> volatilisation from manure can be divided into four categories: meteorological, soil and manure characteristics, and manure application techniques. Among meteorological factors, air temperature, wind speed, solar radiation and vapour pressure deficit (VPD) are the most important (Gordon et al., 2001; Sommer et al. 1991). Among soil and manure factors, soil temperature, soil water content, soil and manure pH, soil texture, total ammoniacal N (TAN) content, and manure dry matter content are of major importance (Gordon and Schuepp, 1994; Moal et al., 1995; Sommer and Olesen, 1991). Among application techniques, rate, placement and timing are the most important (Gordon et al., 2001; Svensson, 1994).

#### 2.3 Nitrous Oxide Emissions

Nitrous oxide (N<sub>2</sub>O) is a greenhouse gas (GHG) produced in soils through the microbial process of nitrification and denitrification (Huang, et al., 2002; IPCC, 1996b; Sharpe and Harper, 1997). Currently, the global mean atmospheric concentration of N<sub>2</sub>O is about 330 parts per billion volume (ppbv), which is 8% greater than pre-industrial era and is increasing at a rate of 0.2-0.3% per year mainly due to anthropogenic activities (Granli and Bøckman, 1994; IPCC, 1996b). Nitrous oxide has 310 times the radiative forcing per molecule relative to CO<sub>2</sub> and a lifetime atmospheric residency of 120-150 years (IPCC, 1996b). Besides being an important GHG, N<sub>2</sub>O is also implicated in the destruction of the stratospheric ozone resulting in an increase in the amount of harmful ultraviolet radiation reaching the surface of the Earth (Ryden et al., 1978; Smith et al., 1998).

The application of N fertiliser and animal manure to fields contributes about 81% of the anthropogenic N<sub>2</sub>O emissions (Isermann, 1994). Field crops uptake only about 50% of the applied N, of which 50% is found in the grain while the rest remains in the crop residue and is returned to the soil (Beauchamp, 1997). Several studies have shown that inorganic N fertiliser application induces N<sub>2</sub>O emissions. For example, MacKenzie et al. (1997) conducted an experiment to test the effect of tillage method, corn-soybean-alfalfa rotations and nitrogen fertilisation on N<sub>2</sub>O emissions and found that inorganic fertiliser application increased N<sub>2</sub>O emissions compared to unfertilised controls. Maggiotto et al. (2000) reported similar results when studying the effects of different forms of N fertiliser application on N<sub>2</sub>O and NO emissions from turf grass. They found that the use of inorganic N fertiliser induced the emissions of both N<sub>2</sub>O and NO compared to zero N fertiliser application.

Organic fertilisers such as animal manures have also been recognised as another major source of  $N_2O$  emissions. The addition of organic fertilisers (manure, crop residue and other organic materials) may result in high  $N_2O$  emissions (Baggs et al., 2002; Bernhard et al., 1999; Burton et al., 1997; Wagner-Riddle et al., 1997). In a study designed to determine the effect of long-term application of manure on  $N_2O$  emissions, Chang et al. (1998) found that continuous application of manure on the same land resulted in higher  $N_2O$  emissions compared to the control (zero manure). Tripling the manure rate resulted in up to 80 times higher  $N_2O$  emissions compared to the control. The addition of organic material to the soil increases the activity of micro-organisms by supplying a large pool of organic C and N and by changing the soil physical and chemical properties which results in large  $N_2O$  emissions (Beauchamp, 1997; Eichner, 1990).

A number of environmental factors and agricultural management practices regulate N<sub>2</sub>O production in soils. These include soil water content; N availability and organic C supply; soil type, pH and soil temperature; and tillage systems (Dobbie and Smith, 2003; Granli and Bøckman, 1994; MacKenzie et al., 1997; Smith et al., 1998; Stevens et al., 1989).

#### 2.4 Nitrate Pollution

Nitrate (NO<sub>3</sub><sup>-</sup>) is a form of nitrogen that is preferentially taken up by plants and it is easily leached by water as it moves through the soil profile thus contaminating subsurface and surface water systems. This may have serious health and environmental implications. When consumed, NO<sub>3</sub><sup>-</sup> may be converted into nitrite (NO<sub>2</sub><sup>-</sup>) in the digestive system of infants thus causing a medical condition known as methemoglobinaemia or blue-baby syndrome, which

can be fatal in some cases. Death may occur due to lack of oxygen in blood (Paul and Clark, 1989). Nitrate leaching occurs mainly in areas where there is excessive moisture coupled with low soil permeability and naturally high water table (Astatkie et al., 2001; FAO, 2001). To reduce the risk of NO<sub>3</sub><sup>-</sup> contamination, Canada and the USA have set a maximum acceptable NO<sub>3</sub><sup>-</sup>-N concentration for drinking water at 10 mg NO<sub>3</sub><sup>-</sup>-N L<sup>-1</sup> (Richards et al., 1990; Jokela, 1992; Health Canada, 2003). Water that has NO<sub>3</sub><sup>-</sup>-N concentration above this limit may be regarded as unsuitable for human consumption. Sources of NO<sub>3</sub><sup>-</sup> in groundwater include decaying organic material such as plants and animals, N fertilisers, manure, and domestic sewage (Paul and Clark, 1989). Nitrogen from both commercial fertiliser and manure is susceptible to leaching through the soil profile as NO<sub>3</sub><sup>-</sup> and may contaminate groundwater (Jokela, 1992). Generally, NO<sub>3</sub><sup>-</sup>-N concentration in the soil profile increases with increase in inorganic N fertiliser rate (Liang and MacKenzie, 1994; Elmi et al., 2000) as well as with increasing manure rate (Jokela, 1992; Angle et al., 1993).

Besides causing health problems, NO<sub>3</sub> losses may also result in eutrophication of rivers and lakes. Together with phosphorus (P), N is the major nutrient required for algae growth in aquatic ecosystems. Decomposing algae depletes dissolved oxygen in water, thus negatively affecting aquatic life and water quality. Moreover, NO<sub>3</sub> is a precursor for N<sub>2</sub>O production under reducing (oxygen-limiting) conditions, which are favourable for denitrification (FAO, 2001; Granli and Bøckman, 1994; Weslien et al., 1998).

#### 2.5 Denitrification and N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> Product Ratios

Denitrification is the process by which fixed N is returned to the atmospheric

dinitrogen (N<sub>2</sub>) pool. The environmental impact of denitrification depends on whether the end product of NO<sub>3</sub>-N reduction is N<sub>2</sub>O or N<sub>2</sub> (Elmi, 2002; Stevens and Laughlin, 2001). Denitrification can affect the environment unfavourably by increasing the N<sub>2</sub>O content of the atmosphere and the denitrifying process in the soil can serve both as a producer and consumer of N<sub>2</sub>O (Paul and Clark, 1989). If denitrification leads to high N<sub>2</sub>O production, the net effect may be trading a water pollutant NO<sub>3</sub>-N, for an air pollutant N<sub>2</sub>O (Lowrance et al., 1998). Denitrification takes place under anaerobic conditions and is dependent on organic C and NO<sub>3</sub> availability (Beauchamp, 1997; Granli and Bøckman, 1994). It is generally agreed that under anaerobic conditions denitrification is the major source of N<sub>2</sub>O emissions in agricultural soils (Granli and Bøckman, 1994). However, both the rate of denitrification and the N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratio must be known in order to evaluate N<sub>2</sub>O emissions through denitrification under anaerobic conditions (Mosier, 1998). Beauchamp (1997) suggested that the N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> product ratios might be as important as the quantities of substrates in determining the proportion of fertiliser N that is emitted as N<sub>2</sub>O, yet few studies have been devoted to the analysis of product ratios. It is worth pointing out that even more lacking is information on the effect of tillage on the N2O:N2O+N2 product ratios following manure application. Moreover, most studies reporting on N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratios were conducted in laboratories (Stevens and Laughlin, 2001; Weier et al., 1993), and therefore it is doubtful whether these results can be directly extrapolated to field conditions.

Similar to denitrification, the N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratio is variable and dependent on microbial population, available C, and soil environmental conditions such as soil water content, temperature, soil pH and substrate availability (Aulakh et al., 1984; FAO, 2001;

Stevens and Laughlin, 2001; Weier et al., 1993). The N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratio can vary widely, and  $N_2O$  or  $N_2$  can in some cases be the sole gaseous product of denitrification (Granli and Bøckman, 1994; Weier et al., 1993). Aulakh et al. (1984) found that the mole fraction of N<sub>2</sub>O varied from 28% to 99% and cautioned against the use of a single N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratio when estimating N<sub>2</sub>O emissions from agricultural soils. They concluded that frequent measurement of the N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratio is necessary for proper N<sub>2</sub>O assessment. Elmi et al. (2003) pointed out that in order to accurately assess the environmental impact of the denitrification process, measurement of the N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratio is necessary. concentration and soil water content influence the N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub>ratio; at high soil NO<sub>3</sub>-N and water contents N<sub>2</sub> is predominant, while at low levels, N<sub>2</sub>O is often dominant (Granli and Bøckman, 1994; Paul and Clark, 1989; Weier et al., 1993). Stevens and Laughlin (2001) suggested that the application of liquid manure would tend to favour N<sub>2</sub> production because it supplies organic C, has high pH and a low NO<sub>3</sub>-N concentration. However, most studies (Burton et al., 1997; Granli and Bøckman, 1994; Sharpe and Harper, 2002; Sherlock et al., 2002) report higher N<sub>2</sub>O emissions following manure application, which suggests higher  $N_2O:N_2O+N_2$  ratio. One of the objectives of this present research was to evaluate the impact of tillage method and manure on denitrification and the N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratio in the field.

#### 2.6 Tillage Systems

No-tillage (NT), also known as zero tillage, is the direct seeding of crops with no previous or subsequent physical disturbance of the soil, while conventional tillage (CT) involves primary and secondary cultivation prior to planting. No-tillage is increasingly being

adopted in Canada (Statistics Canada, 2001) because of its many advantages over CT, which include improved soil structure, higher soil water retention, reduced soil erosion, carbon (C) sequestration and increased crop yields and economic benefit to the producer (Grandy et al., 2006b). The major disadvantage with NT is that it encourages the formation of soil macropores, which may act as conduits for agrochemical movement into ground water (Green et al., 1995). Moreover, there are reports that NT may increase N<sub>2</sub>O and NH<sub>3</sub> emissions and NO<sub>3</sub>-N leaching, however, other reports show the opposite or no difference. For example, MacKenzie et al. (1997; 1998) found higher N<sub>2</sub>O fluxes with NT than CT. Similar findings were reported by Aulakh et al. (1984) and Skiba et al. (2002). On the contrary, Passianoto et al. (2003) reported lower N<sub>2</sub>O emissions with NT compared to CT.

Boddy and Baker (1990) as well as Schreiber and Cullum (1992) reported higher NO<sub>3</sub><sup>-</sup>-N leaching under NT than under CT, while Elmi et al. (2003) found that tillage system had no significant effect on NO<sub>3</sub><sup>-</sup>-N leaching. According to Paul and Clark (1989), good soil conservation practices such as NT systems reduce NO<sub>3</sub><sup>-</sup>-N losses through erosion, but result in higher NO<sub>3</sub><sup>-</sup>-N losses through leaching. Oppositely, NO<sub>3</sub><sup>-</sup>-N leaching has been reported to be higher under CT compared to NT (Angle et al., 1993; Patni et al., 1998; Randall and Iragavarapu, 1995; Thiagarajan, 2005; Varshney et al., 1993). The higher NO<sub>3</sub><sup>-</sup>-N leaching with CT compared to NT was attributed to either greater N mineralisation under CT or greater denitrification under NT. As mentioned before, denitrification is a major process for N<sub>2</sub>O production in soils and its impact on the environment depends on whether its end product is N<sub>2</sub>O or N<sub>2</sub>.

With regard to NH<sub>3</sub> volatilisation, Al-Kanani and MacKenzie (1992) reported higher

losses with NT than CT. Higher NH<sub>3</sub> volatilisation losses from NT are normally attributed to the fact that manure is normally left on the surface i.e., not incorporated, while in CT it is normally incorporated. The conflicting findings emphasise the need for more research on the impact of tillage on N losses. Studies that simultaneously look at the effect of tillage method on N<sub>2</sub>O, NH<sub>3</sub> emission and NO<sub>3</sub>-N leaching as well denitrification and the N<sub>2</sub>O:N<sub>2</sub> ratio following the application of livestock manure are lacking. The current study evaluated all these simultaneously in the same field to identify tradeoffs among these N forms.

#### 2.7 Odour Emissions

Malodours emanating from livestock farms are a major nuisance to the general public. This is more so since towns are slowly encroaching farming areas. Land spreading of slurries and manure, in particular, causes more complaints about nuisance odour than any other stage of livestock production (Williams, 1984; Phillips et al., 1991). Moreover, some components of odours are known to have negative effects on crops, animals and humans. For example, components of odours such as phenols and indoles, inhibit plant growth and cause respiratory problems in livestock, while sulphurous odourants may be a health hazard to humans (Hobbs et al., 1999). Odour dispersion is highly affected by weather conditions, particularly atmospheric stability and wind speed and direction (Guo et al., 2006; Smith and Watts, 1994b). Significant research has been devoted to odour emissions from animal buildings and manure storage facilities; however, odour emissions from field-applied manure have not received adequate attention. Part of this thesis reports on the impact of management practices and meteorological conditions on odour emissions from field-applied hog slurry.

#### **CHAPTER 3**

Ammonia and Nitrous Oxide Emissions from Two Acidic Soils of Nova Scotia

Fertilised with Liquid Hog Manure Mixed With or Without Dicyandiamide

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#### **ABSTRACT**

Gaseous nitrogen (N) loss from field-applied manure in the form of ammonia (NH<sub>3</sub>) and nitrous oxide (N<sub>2</sub>O) has negative agronomic, environmental and health implications. This study was undertaken to evaluate the combined effect of soil type and dicyandiamide (DCD) on NH<sub>3</sub> and N<sub>2</sub>O emissions following application of liquid hog manure. Soil samples (100 g) were placed in 500 mL screw-top Mason-jars and de-ionised water was added to bring the soil samples to 50, 70 and 90% water-filled pore space (WFPS). Slurry and Slurry+DCD treatments were applied at a rate equivalent to 116,000 L ha<sup>-1</sup>. The jars were then sealed and incubated at 21°C for 21 d. Ammonia volatilisation was quantified using boric acid traps while N<sub>2</sub>O gas concentrations were analysed using gas chromatography. Results showed that DCD had no effect (p> 0.05) on either NH<sub>3</sub> or N<sub>2</sub>O emissions. However, soil type had a significant effect (p< 0.05) on both gases. Overall, the Pugwash soil produced 3 and 2.5 times more NH<sub>3</sub> and N<sub>2</sub>O, respectively, than the Acadia soil. N<sub>2</sub>O emissions from both soils increased with an increase in %WFPS, indicating that during the spring and fall in Atlantic Canada, when soils are generally wet, a significant amount of N<sub>2</sub>O may be emitted from these soils. The relationship between cumulative N<sub>2</sub>O and %WFPS was best described by an exponential function  $R^2 = 0.83$  and p<0.05 (both soils). Therefore, soil type should be taken into consideration when formulating N<sub>2</sub>O emission factors. The addition of DCD together with slurry may not be a viable strategy to mitigate N<sub>2</sub>O emissions from acidic soils. To reduce emissions of both gases, livestock slurry should not be applied on wet soils.

#### 3.1 INTRODUCTION

The loss of nitrogen (N) from field-applied manure through ammonia (NH<sub>3</sub>) and nitrous oxide (N<sub>2</sub>O) emission has agronomic, environmental and health implications (FAO, 2001). Ammonia volatilisation is the major gaseous pathway of N loss from livestock manure, and it is estimated that up to 75% of the total NH<sub>3</sub> in manure may be lost within 10 to 15 h following field application (Gordon et al., 2001; Moal et al., 1995). These large NH<sub>3</sub> losses reduce N available for crop use (Moal et al., 1995; Sommer et al., 2003), contribute to acidification and eutrophication of natural ecosystems (FAO, 2001), and also contribute to N<sub>2</sub>O formation (IPCC, 1996b; Ferm, 1998). Nitrous oxide is a greenhouse gas (GHG) produced in soils through nitrification and denitrification (Granli and Bøckman, 1994). Besides being an important GHG, N<sub>2</sub>O is also implicated in the destruction of the ozone layer (Crutzen, 1981; IPCC, 1996b).

Emissions of both NH<sub>3</sub> and N<sub>2</sub>O, during the field application of manure, are influenced by soil type and soil water status. Generally, when soil water content increases NH<sub>3</sub> volatilisation losses also increase due to reduced slurry infiltration (Sommer and Hutchings, 2001; Sommer et al., 2003). Similarly, when soil water content increases N<sub>2</sub>O emissions also increase, mainly as a result of enhanced denitrification. As water-field pore space (WFPS) increases, oxygen diffusion into the soil is reduced creating anaerobic conditions, thus enhancing N<sub>2</sub>O production through denitrification (Granli and Bøckman, 1994; Maag and Vinther, 1999). Nova Scotia is characterised by wet conditions during fall and spring and relatively dry conditions during summer. Animal manure is typically applied in the spring and fall, when soil conditions may enhance NH<sub>3</sub> and N<sub>2</sub>O emissions.

Dicyandiamide (DCD) is a nitrification inhibitor (NI) that has been shown to reduce N<sub>2</sub>O emissions following application of urea (Vallejo et al., 2001; Malla et al., 2005) and animal wastes (de Klein et al., 1996; Di and Cameron, 2003; Di and Cameron, 2005). Vellejo et al. (2005) conducted a field trial and found that mixing pig slurry with DCD lowered N<sub>2</sub>O emissions compared to slurry alone. Similarly, Merino et al. (2002) found that DCD reduced N<sub>2</sub>O emissions from cattle slurry by up to 60% compared to slurry alone. Hatch et al. (2005) reported similar results in a laboratory experiment conducted at air temperature of 10°C (night) and 20°C (day) and lasted for 36 days. The authors found that DCD reduced N<sub>2</sub>O emissions from cattle slurry by 96% compared to the slurry-only treatment. Furthermore, Thompson (1989) found that mixing DCD with cattle slurry reduced denitrification rates from 52 to 6 kg N ha<sup>-1</sup>. Conversely, in a laboratory experiment, Dendooven et al. (1998) reported that mixing DCD with pig slurry had no significant effect on N<sub>2</sub>O production compared to slurry alone. Williamson and Jarvis (1997) reported that DCD reduced N<sub>2</sub>O flux rates from fresh dairy cow urine but not from dung and stored waste water. Meanwhile, Vallejo et al. (2001) found that DCD significantly reduced N<sub>2</sub>O emissions from sandy loam and clay loam soils but not from a sandy clay loam soil after urea application. Besides reducing N<sub>2</sub>O emissions, DCD can also reduce NO<sub>3</sub>-N leaching following field application of animal wastes (Di and Cameron, 2002; Cameron and Di, 2004; Vallejo et al., 2005).

Dicyandiamide retards the rate at which ammonium (NH<sub>4</sub><sup>+</sup>) is converted to nitrate (NO<sub>3</sub><sup>-</sup>), thus increasing NH<sub>4</sub><sup>+</sup> content in the soil. Due to the higher soil NH<sub>4</sub><sup>+</sup> content, some studies suggest that DCD may enhance NH<sub>3</sub> volatilisation (Davies and Williams, 1995; Gioacchini et al., 2002), and hence creating a trade-off. In a rice-wheat system, Banerjee et

al. (2002) found that DCD increased NH<sub>3</sub> volatilization by 7% compared to urea alone, while in a rice only system the losses were statistically similar. Rogers (1983) reported that mixing DCD with urea increased NH<sub>3</sub> volatilisation by up to 70%. However, other studies reported no difference or even lower NH<sub>3</sub> losses. For example, Dendooven et al. (1998) found that DCD reduced NH<sub>3</sub> volatilisation from pig slurry by 17%. Clay et al. (1990) reported lower NH<sub>3</sub> loss from plots receiving urea + DCD compared to urea only. To better understand the nature and extent of this tradeoff between the two gases, it is important to measure emissions of both these gases simultaneously in the system under study. Most of the above mentioned studies only examined the effect of DCD on one gas, and not both at the same time. Furthermore, according to our knowledge, there are no reports that have evaluated the effectiveness of DCD in reducing N<sub>2</sub>O emissions from hog slurry applied to acidic soils.

The objective of this study was to evaluate the combined effects of soil type, soil water status and DCD on  $NH_3$  and  $N_2O$  emissions from hog slurry applied to two acidic soils.

#### 3.2 MATERIALS AND METHODS

#### 3.2.1 Soils Description and Experimental Design

The two soils used in this study were collected from two forage fields (0-20 cm layer) in Great Village, Nova Scotia (45°25′N, 63°36′W). One of the soils is classified as a Pugwash sandy loam (Humo-Ferric Podzol or Orthic Podzol, Canadian and FAO classification) while the other is an Acadia fine loam marine (Gleyed Regosol or Regosol, Canadian and FAO classification) (Agriculture and Agri-food Canada, 1998; Webb, et al., 1991). Pugwash soils are developed from strongly acidic, reddish brown, sandy loam to loam till. Acadia soils

(Marshland) are young soils developed on very strongly to slightly acid deep level silt loam to silty clay loam, marine sediments. Acadia soils were reclaimed from salt marsh and dyked to protect them from tidal flooding.

After collection, the soils were air-dried and passed through a 2 mm sieve. Physical and chemical characteristics of both soils are shown in Table 3.1. The experimental design was a 3-level factorial with two soil types (Pugwash and Acadia), three soil water levels (50, 70 and 90% WFPS) and two manure amendments (Slurry (S) and Slurry+DCD (S+DCD)). The treatments were replicated three times. The hog slurry was obtained from a nearby commercial hog-sow operation and its characteristics are shown in Table 3.1.

## 3.2.2 Soil Water Content Adjustment and Slurry Amendment

A 100 g air-dried sample of each soil was placed in 500 mL wide-mouth screw-top Mason-jars with internal diameter 6.5 cm and de-ionised water was added to bring the WFPS to 30%. The screw-top Mason-jar diffusion unit used in this experiment was similar to that described by Khan et al. (1997, 2001) with slight modifications (Appendix 1). Modifications included fitting a rubber septum for gas sampling. The soil was left in the jars for 2 d (pre-incubation) prior to the addition of the slurry. The soil water content was then adjusted to 50, 70 and 90% WFPS by adding de-ionised water. The hog slurry was surface-applied (not incorporated) at a rate equivalent to 116,000 L ha<sup>-1</sup> (325 kg N ha<sup>-1</sup>), which is double the recommended rate. Dicyandiamide was applied at 30% of the total NH<sub>4</sub><sup>+</sup>-N applied in the slurry, equivalent to 66 kg ha<sup>-1</sup> (double usual rate). Dicyandiamide is normally applied at 10-30 kg ha<sup>-1</sup> (Di and Cameron, 2004). The DCD was suspended in a small amount of water,

shaken and then mixed with the slurry to get a good homogenous mix. No adjustment was made to the slurry rate to take into account the N contained in the DCD. The jars were incubated in the dark at 21 °C for 21 d.

## 3.2.3 Ammonia and N<sub>2</sub>O Measurements

Ammonia volatilisation was measured over 14 d using acid traps that were placed inside the head space of the screw-top Mason-jars (Khan et al., 1997, 2001). After slurry application, Petri dishes containing 5 mL of 4% boric acid (H<sub>3</sub>BO<sub>3</sub>) were attached to the jar lids and the lids were then placed on the jars. The jars were then sealed with metal screw-on bands, thus creating a 400 mL (400 cm<sup>3</sup>) head space. The acid traps were exchanged at 1, 4, 7, 11 and 14 d. Soon after removal, the acid traps were diluted with 5 mL deionised water and NH<sub>3</sub> concentrations analysed by titration with 0.0051 MH<sub>2</sub>SO<sub>4</sub> (Khan et al., 1997, 2001). After the removal of NH<sub>3</sub> traps or after gas sampling the jars were kept open for at least 1 h to replenish oxygen.

Before removing the NH<sub>3</sub> traps, 20 mL gas samples were collected using a 20 mL disposable syringe (Becton-Dickinson, NJ) for N<sub>2</sub>O determination. Gas samples were collected daily for the first week and then at 11, 14, 18 and 21 d after slurry addition. To allow reliable detection of the relatively low rates of N<sub>2</sub>O flux, a long incubation period was chosen. Because of the low rates of N<sub>2</sub>O production, alteration of the soil-atmosphere N<sub>2</sub>O gradient is unlikely nor would significantly altered rates of N<sub>2</sub>O consumption by the soil be anticipated. Prior to gas sampling, the head space was thoroughly mixed by inserting a syringe through the rubber septum and pumping several times. The gas samples were

transferred into pre-evacuated 12 mL glass vials (Labco Exetainer, High Wycombe, UK), which were sealed with silicone to prevent gas leakage and kept until analysis. The N<sub>2</sub>O concentration was analysed using a Varian GP3800 gas chromatograph (GC) fitted with an electron capture detector (Varian Inc., Palo Alto, CA).

### 3.2.4 Statistical Analysis

Both NH<sub>3</sub> and N<sub>2</sub>O data were subjected to analysis of variance (ANOVA) using the PROC GLM function of the SAS statistical programme (SAS Institute, 1996). With regard to N<sub>2</sub>O, data from each sampling day were analysed separately. Unless otherwise stated, differences among treatments were declared to be significant at p< 0.05. Cumulative N<sub>2</sub>O losses were calculated by integrating N<sub>2</sub>O losses measured between sampling periods. Due to high variability and violation of the normality and constant variance assumptions, N<sub>2</sub>O data were log-transformed before analysis. When there was a significant treatment effect, means were compared using Duncan Multiple Range test (DMRT).

## 3.3 RESULTS AND DISCUSSION

### 3.3.1 Ammonia Volatilisation

Overall, the NH<sub>3</sub> volatilisation losses from both soils were low; this is presumably due to the low pH of both soils (4.7 and 5.7), lack of air movement inside the jars and the low pH (6.0) of the slurry. Kissel et al.(1977) showed that for maximum NH<sub>3</sub> loss the air exchange in the chamber should be 14 volumes min<sup>-1</sup>. Similarly, Fenn and Kissel (1973) observed that NH<sub>3</sub> loss reached a maximum at air exchange of 14 to 16 volumes min<sup>-1</sup>. Air removes the

NH<sub>3</sub>-laden layer, thus diminishing the NH<sub>3</sub> partial pressure above the soil and increasing NH<sub>3</sub> volatilisation (Sommer and Olesen, 2000; Huijsmans et al., 2003). In the current study there was no air exchange in the jars, which may have contributed to the low NH<sub>3</sub> losses. Moreover, when the slurry was applied it quickly infiltrated into the soil, thus reducing NH<sub>3</sub> volatilisation. Slurry infiltration into the soil reduces the pool of N (NH<sub>4</sub><sup>+</sup>+NH<sub>3</sub>) at the soil surface and thus lowering NH<sub>3</sub> volatilisation (Sommer et al., 2003). Furthermore, the low pH (6.0) of the slurry used in the study might have also contributed to the low NH<sub>3</sub> volatilisation (Stevens et al., 1989; Sommer and Hutchings, 1995). Low slurry pH shifts the acid-base equilibrium from NH<sub>3</sub> to NH<sub>4</sub><sup>+</sup>, thus reducing NH<sub>3</sub> volatilisation. In addition, the low pH (4.7 and 5.7) of the soils used in the study may have reduced NH<sub>3</sub> volatilisation (Genermont and Cellier, 1997; Sommer et al., 2003).

On average, NH<sub>3</sub> losses ranged from 0.1 to 0.29 mg kg<sup>-1</sup> soil, representing 0.36 to 1% of the applied N (Table 3.2). Sigunga et al. (2002) recorded NH<sub>3</sub> losses amounting to < 0.3% of fertiliser N applied from soils at pH of 6.0 and 6.1. Clough et al. (2003) recorded NH<sub>3</sub> losses ranging from 1.2 to 7.9% of urine N applied at soil pH 4.7 and 7.7, respectively. Statistical analysis showed that soil type had a significant effect (p<0.05) on NH<sub>3</sub> volatilisation (Table 3.2). The Pugwash soil had the largest NH<sub>3</sub> losses, which were 3 times higher than those from the Acadia soil.

The higher NH<sub>3</sub> volatilisation losses from the Pugwash soil are presumably the result of the higher pH (5.7). Results agree with those reported by Sigunga et al. (2002) when comparing NH<sub>3</sub> loss from soils with pH values ranging from 6.0 to 7.7. Soil pH is known to have a significant influence on NH<sub>3</sub> volatilisation, such that an increase in soil pH results in

an increase in NH<sub>3</sub> volatilisation. This can be attributed to the acid-base equilibrium shifting from NH<sub>4</sub><sup>+</sup> to NH<sub>3</sub> form and thereby increasing NH<sub>3</sub> losses (Genermont and Cellier, 1997; Sommer and Olesen, 2000).

The amendments (S and S+DCD) had no effect (p> 0.05) on NH<sub>3</sub> volatilisation, implying that mixing slurry with DCD did not increase NH<sub>3</sub> volatilisation. On average, 0.2 mg N kg<sup>-1</sup> soil was lost from both S and S+DCD, accounting for 0.7% of applied N (Table 3.2). The results concur with Clay et al. (1990) who reported no difference in NH<sub>3</sub> volatilisation after applying urea and urea+DCD to bare soil. Meanwhile, Dendooven et al. (1998), observed 17% lower NH<sub>3</sub> volatilisation rate from soil amended with pig slurry+DCD than soil amended with slurry alone. Similarly, Gioacchini et al. (2002) found that mixing DCD with urea reduced NH<sub>3</sub> volatilisation compared to urea alone. On the contrary, Banerjee et al. (2002) found that in a rice-wheat system, urea + DCD plots lost 7% more NH<sub>3</sub> compared to urea only plots, while losses in a rice system were statistically similar.

Soil water content had no effect (p> 0.05) on NH<sub>3</sub> volatilisation (Table 3.2). On average, losses were 0.2 mg N kg<sup>-1</sup> soil, accounting for 0.7% of applied N. It was surprising that soil water content had no effect on NH<sub>3</sub> volatilisation. This is contrary to other studies which reported higher NH<sub>3</sub> losses from soils receiving inorganic fertiliser (Sigunga et al., 2002) and animal slurry (Sommer et al., 2003) as soil water content increased. Sogaard et al. (2002) when using a model, found that on average 10% more NH<sub>3</sub> was volatilised from animal slurry applied on wet soils compared to that applied to dry soils. Results of the current study suggest that under acidic soil conditions, soil pH is the major variable controlling NH<sub>3</sub> volatilisation, with soil water content playing a secondary role. However, the increase in soil

water content might have promoted other N loss pathways such as denitrification. Thus, it is also important to assess these potential loss mechanisms.

### 3.3.2 Nitrous Oxide Emissions

## 3.3.2.1 Daily N<sub>2</sub>O Evolution

Nitrous oxide evolution started soon after slurry application, reached a maximum 1 to 2 d after application, and then declined to minimum levels by 4 to 5 d (Figure 3.1). Previous studies (Maag and Vinther, 1999; Flessa and Beese, 2000) have shown similar rapid increases of N<sub>2</sub>O fluxes following livestock slurry application, and attributed this to enhanced denitrification driven by easily available N, C, and saturated soil conditions. A maximum flux of 1.9 mg N<sub>2</sub>O kg<sup>-1</sup> soil d<sup>-1</sup>, associated with the highest soil water content (90% WFPS), was observed 1 d after slurry application, indicating that most of the N<sub>2</sub>O produced was as a result of denitrification. The addition of DCD had no significant (p> 0.05) effect on N<sub>2</sub>O flux throughout the measurement period. However, soil type had a significant (p< 0.05) effect on N<sub>2</sub>O fluxes on d 1, 2 and 14. Meanwhile, the soil water content and the soil type×soil water content interaction had a significant (p< 0.05) effect on daily N<sub>2</sub>O fluxes on d 1 and 2 (Table 3.3).

### 3.3.2.2 Cumulative N<sub>2</sub>O Emissions

Soil type had a significant (p< 0.05) effect on cumulative  $N_2O$  emissions, with the Pugwash soil emitting higher  $N_2O$  compared to the Acadia soil (Table 3.2). On average, cumulative  $N_2O$  losses over the 21 d of the study were 1.09 mg  $N_2O$ -N kg<sup>-1</sup> soil for the

Pugwash soil and 0.46 mg N<sub>2</sub>O-N kg<sup>-1</sup> soil for the Acadia soil, accounting for 3.9% and 1.64% of applied slurry N, respectively. In a field experiment, Vallejo et al. (2005) found total N<sub>2</sub>O losses ranging from 0.46 to 1.05 g N m-<sup>2</sup>; these losses accounted for 0.5 to 2.95% of N applied as pig slurry. Meanwhile in a field experiment, Watanabe et al. (1997) recorded total N<sub>2</sub>O-N losses amounting to 0.085% and 0.098% of total N applied as cattle and swine excreta, respectively. The much higher N<sub>2</sub>O emissions from the Pugwash soil were presumably caused by the higher soil pH, which might have been more suitable for denitrifier organisms thus enhancing denitrification (Granli and Bøckman, 1994). The study suggests that soil type plays a major role in N<sub>2</sub>O production and therefore has to be taken into consideration when developing N<sub>2</sub>O emissions factors.

Dicyandiamide had no significant (p>0.05) effect on cumulative N<sub>2</sub>O emissions (Table 3.2). On average, the S treatment emitted 0.83 mg N<sub>2</sub>O-N kg<sup>-1</sup> soil, while the S+DCD treatment emitted 0.72 mg N<sub>2</sub>O-N kg<sup>-1</sup>, representing 2.95 and 2.59% of applied N, respectively. These findings are in agreement with Williamson and Jarvis (1997) who found no difference in N<sub>2</sub>O emissions when DCD was added to dung and stored wastewater. Meanwhile, Merino et al. (2001) reported that DCD lowered N<sub>2</sub>O emissions compared to cattle slurry alone, but the difference was not significant. Mosier et al. (1998) found that in acidic soils DCD did not inhibit N<sub>2</sub>O emissions and concluded that under acidic conditions, DCD was inactivated by binding to humic compounds.

On the contrary, Di and Cameron (2002; 2005) and Merino et al (2002) found that DCD reduced N<sub>2</sub>O emissions when added to cattle urine and cattle slurry, respectively. Also, Hatch et al. (2005) reported that mixing DCD with cattle slurry reduced N<sub>2</sub>O emissions by

96% compared to slurry only. The contrasting results are not entirely unexpected since the effectiveness of DCD is known to be highly dependent on soil and environmental factors such as temperature (Davies and Williams, 1995; Prasad and Power, 1995). Most NIs including DCD are more effective at temperatures <20°C (Prasad and Power, 1995). Di and Cameron (2004) showed that DCD degrades faster at air temperature of 20°C compared to 8°C, and hence decreasing its inhibitory effect. This study was conducted at 21°C, which might have increased the rate of DCD degradation, thus reducing its effectiveness. Hatch et al. (2005) postulated the following reasons for failure of inhibitors to reduce N2O emissions: (i) inhibitors in some soils may be degraded too fast, (ii) there could be physical separation of inhibitor and N source, and (iii) the inhibitor may not infiltrate all active nitrification sites. In addition, the high organic matter content [Acadia soil (6.5%), Pugwash soil (4.3%)] of both soils used in the current study may have impacted negatively on the inhibitory effect of DCD. When soil organic matter is ≥5% the inhibitory effect of NIs ceases due to the effect of organic matter on sorption and the rate of decomposition of NIs (Prasad and Power, 1995). Combinations of the above may have contributed to the failure of DCD to reduce N<sub>2</sub>O emissions in our study. The results of our study therefore, imply that under the conditions of our study mixing DCD with hog slurry that is to be applied to acidic soil may not be an effective strategy for mitigating N<sub>2</sub>O emissions.

Soil water content had a significant effect (p< 0.05) on cumulative  $N_2O$  emissions (Table 3.2). Cumulative  $N_2O$  emissions increased as the soil water content increased from 50 to 90% WFPS, in agreement with Dobbie and Smith, (2001) and Clough et al. (2004). Generally, increasing soil water content enhances denitrification and thus more  $N_2O$  is

emitted. Maximum  $N_2O$  emissions normally occur at a soil water content where both nitrification and denitrification can proceed simultaneously, which is usually between 45 to 75% WFPS (Granli and Bøckman, 1994). The relationship between cumulative  $N_2O$  and WFPS (both soils) was best described by an exponential function ( $R^2 = 0.83$ , p< 0.05 for both soils) (Figure 3.2), in line with observations reported by Dobbie and Smith (2001) and Clough et al. (2004). This shows that 83% of the variability in  $N_2O$  emissions can be explained by change in WFPS. On average, 0.23, 0.57 and 1.52 mg  $N_2O$ -N kg<sup>-1</sup> soil were emitted from soils with water contents of 50, 70 and 90% WFPS, respectively. These losses accounted for 0.83, 2.04 and 5.44% of applied slurry N, respectively. The fact that the highest  $N_2O$  emissions were associated with the highest soil water content suggests that most of the  $N_2O$  produced was as a result of denitrification. The implication of this result is that during the spring and fall in Nova Scotia, when soils are generally wet, a significant amount of  $N_2O$  may be emitted from these soils.

#### 3.4 CONCLUSIONS

The study has demonstrated that both the Pugwash and Acadia soils have a high potential to produce  $N_2O$ , particularly when wet. Soil type has a significant role on  $NH_3$  and  $N_2O$  emissions, with the highest emissions of both gases associated with the Pugwash soil. The Pugwash soil emitted 2.9 times more  $NH_3$  and 2.4 times more  $N_2O$  compared to the Acadia soil. Under the conditions of the current study, mixing DCD with liquid hog manure to mitigate  $N_2O$  emissions from these soils may not be a viable strategy. The emissions of both gases can be minimised by avoiding spreading livestock slurry on wet soils. Generally,

emissions of both gases can be reduced by using recommended N rates and proper slurry/manure application timing. Long-term field studies are needed to quantify and better understand the factors that govern N losses under acidic soil conditions.

**Table 3.1.** Chemical and physical characteristics of the soils (0-20 cm depth) and liquid hog manure (slurry) used in the study.

Characteristic	Pugwash Soil	Acadia Soil	Hog Slurry
pН	5.69#	4.71*	6.02
TN (%)	0.22	0.33	0.28
Organic Carbon (%)	2.43	3.80	1.20
C:N ratio	11.0	11.5	4.29
NH <sub>4</sub> (%)	nd	nd	0.19
NO <sub>3</sub> (mg kg <sup>-1</sup> )	1.05	2.23	nd
Dry Matter (%)	na	na	3.13
Porosity (%)	58.1	58.5	na
Bulk Density (Mg m <sup>-3</sup> )	1.11	1.10	na
Organic Matter (%)	4.30	6.50	na
CEC (meq/100g)	15.9	14.1	na

nd = not determined, na = not applicable, \*pH 1:2 dry soil: de-ionised water, TN and C determined using CNS analyser.

**Table 3.2.** Impact of soil type, amendment and soil water content (%WFPS) on total  $NH_3$  losses and cumulative  $N_2O$  emissions over a 21-d measurement period.

Treatment		NH <sub>3</sub> -N loss	N <sub>2</sub> O-N loss
		(mg kg <sup>-1</sup> soil)	(mg kg <sup>-1</sup> soil)
Soil type	Acadia	0.10 b	0.46 b
	Pugwash	0.29 a	1.09 a
Amendment	S	0.20 a	0.83 a
	S+DCD	0.20 a	0.72 a
WFPS	50%	0.18 a	0.23 с
	70%	0.19 a	0.57 b
	90%	0.22 a	1.52 a

Means followed by the same letter within the same column and each treatment are not significantly different (p > 0.05) using DMRT.

Table 3.3. Summary of the analysis of variance (ANOVA) for the effects of soil type, soil water content (WFPS), and amendment (Amend) on daily  $N_2O$  fluxes during selected days.

Source of variation	P values				
	Day 1	Day 2	Day 7	Day 14	Day 21
Soil	<0.001*	0.009*	0.078	0.004*	0.981
WFPS	<0.001*	0.001*	0.091	0.38	0.49
Amend	0.282	0.364	0.132	0.642	0.601
Soil×WFPS	<0.001*	0.007*	0.111	0.961	0.866
Soil×Amend	0.406	0.296	0.125	0.621	0.467
WFPS×Amend	0.474	0.805	0.161	0.409	0.402
Soil×WFPS×Amend	0.372	0.369	0.166	0.358	0.058

<sup>\*</sup> Significant at (p< 0.01).

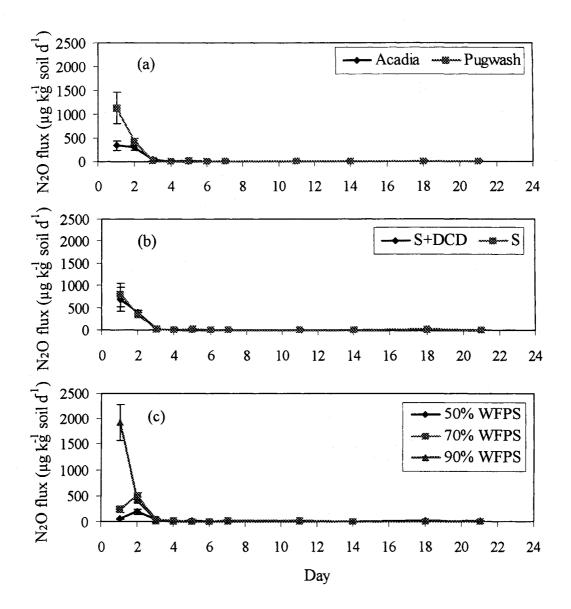


Figure 3.1. Mean daily  $N_2O$  evolution as impacted by (a) soil type (Pugwash and Acadia), (b) amendment (Slurry and Slurry+DCD) and (c) soil water content (%WFPS) over a 21-d measurement period. Vertical bars represent  $\pm$  standard error of mean (n = 3) (note, some error bars are smaller than symbols).

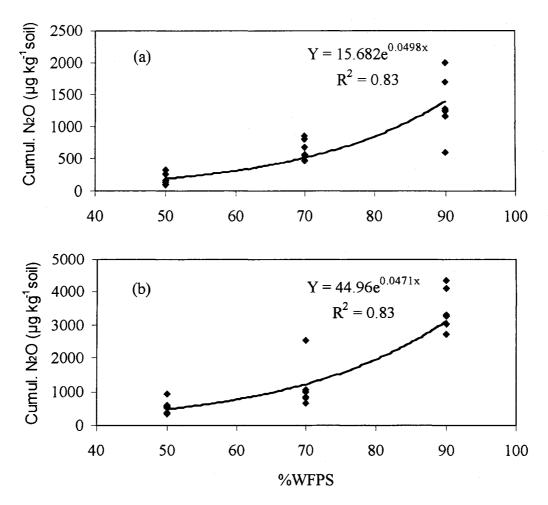


Figure 3.2. Exponential relationship between soil water content (%WFPS) and cumulative  $N_2O$  emissions for (a) Acadia soil and (b) Pugwash soil. In both soils, 83% of the variability in cumulative  $N_2O$  emissions can be explained by the change in %WFPS.

## **CHAPTER 4**

Effect of Lime, Dicyandiamide and Soil Water Content on Ammonia and Nitrous
Oxide Emissions Following Application of Liquid Hog Manure to a Marshland So

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#### **ABSTRACT**

The loss of nitrogen (N) from field-applied manure through ammonia (NH<sub>3</sub>) and nitrous oxide (N<sub>2</sub>O) emissions is of major environmental concern. Both lime and dicyandiamide (DCD) have been suggested as amendments that can mitigate N<sub>2</sub>O emissions, but simultaneously increase the risk of NH<sub>3</sub> volatilisation. This study evaluated the impact of lime and DCD on NH<sub>3</sub> and N<sub>2</sub>O emissions following application of liquid hog manure. Hydrated lime (Ca(OH)<sub>2</sub>) was added to an acidic soil to achieve three pH levels (4.7, 6.3 and 7.4). Soil samples (100 g) were then placed in 500 mL Mason-jars and de-ionised water was added to bring the samples to 50, 70 and 90% water filled pore space (WFPS). Slurry and Slurry+DCD was applied at a rate equivalent to 116,000 L ha<sup>-1</sup>, while DCD was applied at 30% of NH<sub>4</sub>-N applied. Jars were sealed and incubated at 21°C for 21 d. Ammonia volatilisation was quantified using boric acid traps, while N<sub>2</sub>O gas concentration was analysed using gas chromatography. Dicyandiamide had no effect (p> 0.05) on either NH<sub>3</sub> or N<sub>2</sub>O emissions. Both NH<sub>3</sub> and N<sub>2</sub>O emissions increased (p<0.05) as WFPS increased, with emissions ranging from 0.92 to 1.38 kg NH<sub>3</sub> ha<sup>-1</sup> and 123 to 353 g N<sub>2</sub>O-N ha<sup>-1</sup>, respectively. Liming decreased  $(p < 0.01) N_2O$  emissions (547 to 46 g  $N_2O-N$  ha<sup>-1</sup>), but increased (p< 0.05%) NH<sub>3</sub> volatilisation (0.36 to 1.92 kg NH<sub>3</sub> ha<sup>-1</sup>). Results suggest that liming to a pH  $\geq$  6.3 can reduce N<sub>2</sub>O emissions, however, this reduction will be accompanied by a substantial loss of NH<sub>3</sub>.

#### **4.1 INTRODUCTION**

Livestock manure is a valuable source of plant nutrients. However, if poorly managed it can have substantial negative environmental impacts. A major environmental concern associated with manure is loss of nitrogen (N) through nitrate (NO<sub>3</sub>) leaching, ammonia (NH<sub>3</sub>) volatilisation and nitrous oxide (N<sub>2</sub>O) emissions.

Ammonia volatilisation has long been recognised as the major pathway of N loss from livestock manure. It is estimated that up to 75% of total NH<sub>3</sub> in manure may be lost within 10 to 15 h following field-application (Gordon et al., 2001; Moal et al., 1995). These losses reduce the N available for plant uptake, contribute to environmental degradation (including acidification and eutrophication of natural ecosystems) and cause air pollution (Moal et al., 1995; Sharpe and Harper, 2002; Sommer et al., 2003). Moreover, NH<sub>3</sub> can also be oxidised to NO<sub>3</sub><sup>-</sup> and then transformed into N<sub>2</sub>O through denitrification, and this constitutes about 5% of the global N<sub>2</sub>O emissions (Ferm, 1998).

Nitrous oxide is a greenhouse gas (GHG) produced in soils through the microbial processes of nitrification and denitrification (Dalal et al, 2003; Granli and Bøckman, 1994). Besides being an important GHG, N<sub>2</sub>O is also implicated in the destruction of the ozone layer (Bouwman, 1990; Crutzen, 1981). Agriculture, and in particular the field application of N fertilisers and animal manures contribute approximately 81% of the anthropogenic N<sub>2</sub>O emissions (Isermann, 1994).

Soil pH and water content have significant effect on NH<sub>3</sub> volatilisation and N<sub>2</sub>O emissions. As the soil pH increases NH<sub>3</sub> volatilisation also increases due to a higher concentration of dissolved NH<sub>3</sub> in the slurry soil mixture (Sogaard et al., 2002; Sommer and

Olesen, 2000; Sommer et al., 2003). Likewise, as the soil water content increases NH<sub>3</sub> volatilisation also increases as a result of lower slurry infiltration and therefore greater exposure of slurry to the atmosphere (Sigunga et al., 2002; Sogaard et al., 2002; Sommer and Olesen, 2000).

Soil pH affects N<sub>2</sub>O production through its effect on nitrification and denitrification. Generally, both nitrification and denitrification rates increase as soil pH increases (Dalal et al, 2003; Granli and Bøckman, 1994). Some studies however, have shown that both nitrification and denitrification can take place at low soil pH (Bauhus et al., 1996; Granli and Bøckman, 1994; Simek and Cooper, 2002). Moreover, some studies have reported higher N<sub>2</sub>O:N<sub>2</sub> ratios as the soil pH decreases (Nagele and Conrad, 1990; Weier and Gilliam, 1986). Meanwhile, N<sub>2</sub>O emissions generally increase with increase in soil water content. As soil water contents increase, nitrification (an aerobic process) decreases and denitrification (an anaerobic process) increases. According to Granli and Bøckman (1994), maximum N<sub>2</sub>O emissions occur at soil water contents where both nitrification and denitrification can proceed, which is normally between 45 and 75% water-filled pore space (WFPS).

The majority of soils in Nova Scotia, Canada are acidic and therefore, liming of pastures and cultivated fields is a common practice to enhance nutrient availability and reduce aluminium toxicity. Both lime and nitrification inhibitors (NIs), in particular dicyandiamide (DCD) have been suggested as amendments that have a potential to mitigate N<sub>2</sub>O emissions following fertiliser and/or animal waste applications (Clough et al., 2003, 2004; Di and Cameron, 2003; Hatch et al., 2005; Klein et al., 1996; Malla et al., 2005; McTaggart et al., 1997; Merino et al., 2002). Some studies, however, have shown that DCD may not be

effective in mitigating N<sub>2</sub>O emissions from applied manure (Williamson and Jarvis, 1997) and its effectiveness depends on soil and environmental factors (Prasad and Power, 1995; Vallejo et al., 2001).

Liming increases soil pH, which in turn stimulates nitrification and denitrification and subsequently greater conversion of N<sub>2</sub>O to N<sub>2</sub> (Clough et al., 2003; Granli and Bøckman, 1994). Weier and Gilliam (1986), suggested that liming soil to pH> 6.5 may help reduce N<sub>2</sub>O emissions but would decrease the N use efficiency by crops due to higher loss of N as N<sub>2</sub>. Clough et al. (2004), further suggested that liming may reduce N<sub>2</sub>O emissions when soils are at field capacity but may enhance N<sub>2</sub>O and N<sub>2</sub> emissions when soils are wetted beyond field capacity.

Dicyandiamide is a nonvolatile chemical that retards the microbial conversion of ammonium (NH<sub>4</sub><sup>+</sup>) to nitrate (NO<sub>3</sub><sup>-</sup>) and subsequently to the gases, N<sub>2</sub>O and N<sub>2</sub> and thus increasing N-use efficiency (Prasad and Power, 1995). Dicyandiamide inhibits the first stage of nitrification (i.e. oxidation of NH<sub>4</sub><sup>+</sup> to NO<sub>2</sub><sup>-</sup>), by rendering the bacteria's enzymes ineffective (Di and Cameron, 2003). However, due to its mode of action, some studies suggest that DCD may increase NH<sub>3</sub> volatilisation (Banerjee et al., 2002; Davies and Williams, 1995; Gioacchini et al., 2002; Rogers, 1983) thus, creating a tradeoff between N<sub>2</sub>O and NH<sub>3</sub>. Hatch et al. (2005), suggested that the use of NIs to reduce N<sub>2</sub>O emissions has to be evaluated in the widest possible context, since preserving slurry-N as NH<sub>4</sub><sup>+</sup> may increase NH<sub>3</sub> volatilisation.

There is limited information on the impact of soil pH, water content and DCD on  $NH_3$  and  $N_2O$  emissions following the application of liquid hog manure. The objective of this study

was therefore to evaluate the combined effect of lime and DCD on NH<sub>3</sub> and N<sub>2</sub>O emissions from soils of different water contents fertilised with liquid hog manure.

#### 4.2 MATERIALS AND METHODS

### 4.2.1 Soil Description and Experimental Design

The soil (0-20 cm layer) used in this study was collected from a forage field in Great Village, Nova Scotia (45°25′N, 63°36′W). After collection, the soil was air-dried and passed through a 2 mm sieve. The soil is classified as an Acadia fine loam (Gleyed Regosol or Regosol, Canadian and FAO classification) developed on very strongly to slightly acid deep level silt loam to silty clay loam, marine sediments (Agriculture and Agri-food Canada, 1998; Webb et al., 1991). Acadia soils were reclaimed from salt marsh and dyked to protect them from tidal flooding. Chemical and physical characteristics of the soil are shown in Table 4.1.

The experimental design was a factorial with three soil pH levels (4.7, 6.3 and 7.4), three soil water levels (50, 70 and 90% WFPS) and two manure amendments (Slurry (S) and Slurry+DCD (S+DCD)). The amount of water added to bring the soil to the required WFPS was calculated after packing the soil to a bulk density of 1.10 Mg m<sup>-3</sup>, which was similar to that found in the field. The treatments were replicated three times and randomly arranged within each block.

### 4.2.2 Soil pH Adjustment

To achieve pH levels of 4.7, 6.3 and 7.4, hydrated lime (Ca(OH)<sub>2</sub>) was added to dry soil at rates of 0, 4.49 and 7.30 g kg<sup>-1</sup> soil (equivalent to 0, 8.5 and 13.9 t ha<sup>-1</sup>), respectively.

A 100 g sample of lime-treated soil was then placed in 500 mL wide-mouth Mason-jars with internal diameter 6.5 cm. De-ionised water was added to bring the WFPS to 30%. The air tight Mason-jar diffusion unit used in this experiment was similar to that described by Khan et al. (1997, 2001), but also included a rubber septum for gas sampling (Appendix 1). The soil was left in the jars for 8 d (pre-incubation) prior to the addition of the slurry to stabilise the pH and also initiate microbial activity in order to reduce N<sub>2</sub>O peaks due to readily available N and C. The soil pH was monitored throughout the pre-incubation period using a pH meter and subsamples of soils treated and incubated separately under similar conditions. After 8 d the pH had reached constant values.

### 4.2.3 Soil Water Content Adjustment and Slurry Amendment

After the 8 d pre-incubation, the water content was adjusted to 50, 70 and 90% WFPS by adding 15.3, 27.4 and 39.5 mL of de-ionised water, respectively. The amount of water used to raise the soil water content to the required WFPS was adjusted taking into consideration that slurry also contained water. The slurry was surface-applied to the soil (not incorporated) at a rate of 10 mL jar<sup>-1</sup> (116,000 L ha<sup>-1</sup>) amounting to 325 kg N ha<sup>-1</sup>, which is double the recommended rate. The slurry was obtained from a nearby commercial hog-sow operation and its characteristics are shown in Table 4.1. Dicyandiamide was applied at 66 kg ha<sup>-1</sup> (double the frequently used rate). Dicyandiamide is mostly applied at 10-30 kg ha<sup>-1</sup>, however, the effective application rate is not known, especially where high N rates have been applied (Di and Cameron, 2004). We used double DCD rate because manure rate was also doubled. The DCD was suspended in a small amount of water, shaken and then added to the

slurry to get a good homogenous mix. No adjustment in the slurry N rate was made to allow for the N present in DCD (66%). The jars were then incubated in the dark at 21°C for 21 d. During the summer (June-August), average daily maximum temperature in Nova Scotia ranges from 19.5 to 24.8°C, while minimum temperature ranges from 7.9 to 12.4°C.

### 4.2.4 Ammonia and N<sub>2</sub>O Measurements

Ammonia volatilisation was monitored for 14 days using acid traps that were placed inside the head space of the Mason-jars as described by Khan et al. (1997, 2001). After slurry application, Petri dishes containing 5 mL of 4% boric acid (H<sub>3</sub>BO<sub>3</sub>) were attached to the jar lids and the lids were then placed on the jars. The jars were then tightly sealed with metal screw-on bands, thus creating a head space. The acid traps were replaced/removed at 3, 7 and 14 d. Soon after removal, the acid traps were diluted with 5 mL deionised water and thereafter NH<sub>3</sub> concentrations from the traps were analysed by titration with 0.0051 M H<sub>2</sub>SO<sub>4</sub> (Khan et al.,1997, 2001). The amount of NH<sub>3</sub> volatilised was calculated on the basis of soil surface area in the jars. After the removal of NH<sub>3</sub> traps the jars were kept open for at least 1 h to replenish oxygen.

Before removing the NH<sub>3</sub> traps, 20 mL jar head space gas samples were collected using a plastic disposable syringe for N<sub>2</sub>O determination. Gas samples were collected at 1, 2, 3, 5, 7, 11, 14, 18 and 21 d after slurry addition. Prior to gas sampling, the head space was thoroughly mixed by inserting a syringe through the rubber septum and pumping several times. The gas samples were transferred into pre-evacuated 12 mL glass vials (Labco Exetainer, High Wycombe, UK), which were sealed with silicone to prevent gas leakage and

kept until analysis. The N<sub>2</sub>O concentration was analysed using a Varian GP3800 gas chromatograph (GC) fitted with an electron capture detector (Varian Inc., Palo Alto, CA).

#### 4.2.5 Statistical Analysis

Both  $NH_3$  and  $N_2O$  data were subjected to analysis of variance (ANOVA) using the PROC GLM function in SAS (SAS Institute, 1996). Unless otherwise mentioned, differences among treatments were declared to be significant at p<0.05. With respect to  $N_2O$ , data from each sampling day were analysed separately. Cumulative  $N_2O$  losses were calculated by integrating  $N_2O$  losses measured between sampling periods. Due to high variability and violation of the normality and constant variance assumptions,  $N_2O$  data were log-transformed before analysis. When there was a significant treatment effect, means were compared using Duncan Multiple Range test (DMRT).

#### 4.3 RESULTS AND DISCUSSION

### 4.3.1 Ammonia Volatilisation

## 4.3.1.1 Effect of Amendment on NH<sub>3</sub> volatilisation

When averaged across all soil water and pH levels, amendment (S and S+DCD) had no significant effect (p> 0.05) on NH<sub>3</sub> volatilisation (Table 4.2) with an average 1.1 kg NH<sub>3</sub> ha<sup>-1</sup> volatilised representing 0.5% of NH<sub>4</sub><sup>+</sup>-N applied. Under rice growing conditions, Banerjee et al. (2002) found no difference in NH<sub>3</sub> loss between urea and urea+DCD treated plots. Clay et al. (1990), reported similar findings when applying urea and urea+DCD on bare soil. Dendooven et al. (1998), reported lower NH<sub>3</sub> volatilisation from soil amended with pig

slurry + DCD compared with soil amended with slurry alone. Other researchers however, have reported higher NH<sub>3</sub> volatilisation losses when inorganic fertiliser was mixed with DCD compared to fertiliser alone (Davies and Williams, 1995; Gioacchini et al., 2002). Rogers (1983) found that mixing DCD with urea increased NH<sub>3</sub> volatilisation by up to 70%. Nonetheless, results from this study indicate that DCD when mixed with pig slurry has no apparent effect on NH<sub>3</sub> volatilisation.

### 4.3.1.2 Effect of Soil Water Content on NH<sub>3</sub> volatilisation

Ammonia volatilisation was greater at 90% WFPS than at 70 or 50% WFPS, with the latter two not differing significantly from each other (Table 4.2). These results agree with Sigunga et al. (2002) who reported an increase in NH<sub>3</sub> volatilisation as soil water content increased. According to Sogaard et al. (2002), NH<sub>3</sub> loss from slurry applied to wet soil is at least 10% higher than that applied to dry soil. In the current study, 50% more NH<sub>3</sub> was lost from the soil with the highest water content (90% WFPS) compared to the soil at 50% WFPS. This enhanced NH<sub>3</sub> loss has been attributed to reduced slurry infiltration rates in the wetter soils (Sommer and Olesen, 2000; Sommer et al., 2003). Lower infiltration rates enhance volatilisation by lowering resistance to diffusion from soil to the atmosphere. Results of the current study imply that applying livestock slurry soon after heavy rains will result in higher NH<sub>3</sub> volatilisation losses than when applied on dry soil. Such conditions (excessively wet) are normally experienced during fall and spring in Atlantic Canada.

## 4.3.1.3 Effect of Liming (soil pH) on NH<sub>3</sub> volatilisation

Liming had a significant effect (p< 0.05) on NH<sub>3</sub> volatilisation. The soil with the highest pH (7.4) had the greatest NH<sub>3</sub> loss (1.9 kg NH<sub>3</sub> ha<sup>-1</sup>) represented 0.9% of NH<sub>4</sub><sup>+</sup>-N applied (Table 4.2). At soil pH 6.3, 1.0 kg NH<sub>3</sub> ha<sup>-1</sup> was volatilised, while at a pH of 4.7 only 0.4 kg NH<sub>3</sub> ha<sup>-1</sup> was volatilised. Previous studies have shown that NH<sub>3</sub> loss increases with an increase in soil pH (Sigunga et al., 2002, Sommer et al., 2003). Clough et al. (2003) also reported significantly higher NH<sub>3</sub> fluxes at soil pH of 7.7 following urine application to a soil adjusted with quick lime. They found that on average 1.98% (range of 0.79-3.27%) of total N applied was lost through NH<sub>3</sub> volatilisation. This can be attributed to the acid-base equilibrium shifting from NH<sub>4</sub><sup>+</sup> to NH<sub>3</sub> form and thereby increasing NH<sub>3</sub> losses (Clough et al., 2003; Genermont and Cellier, 1997; Sommer and Olesen, 2000).

The low NH<sub>3</sub> losses from the present study, even at the highest soil pH (7.4), might be attributed to lack of air movement in the jars. Air removes the NH<sub>3</sub>-laden layer, thus diminishing the NH<sub>3</sub> partial pressure above the soil and increasing NH<sub>3</sub> volatilisation (Huijsmans et al., 2003; Sommer and Olesen, 2000). In addition, the low pH (6.0) of the slurry used may have also contributed to the low NH<sub>3</sub> losses. Stevens et al. (1989) found that acidifying slurry to pHs of 6.0 and 5.5 reduced NH<sub>3</sub> volatilisation by 83% and 95%, respectively, compared to slurry at pH 7.8. Acidifying slurry shifts the acid-base equilibrium from NH<sub>3</sub> to NH<sub>4</sub><sup>+</sup>, thus reducing NH<sub>3</sub> volatilisation.

#### 4.3.2 Nitrous Oxide Emissions

# 4.3.2.1 Daily N<sub>2</sub>O Evolution

Regardless of treatment, the N<sub>2</sub>O evolution started soon after application of amendments (S and S+DCD), reached maximum after 1 to 2 days (Figure 4.1). Fluxes decreased to minimum levels by day 5. Previous incubation studies have shown that high N<sub>2</sub>O fluxes generally occur soon after livestock slurry application and last for a few days and then decline to background levels (Flessa and Besse, 2000; Maag and Vinther, 1999; Velthof et al., 2003). Similar findings to this study have also been reported following field-application of hog slurry (Chadwick et al., 2000; Rochette et al., 2004; Sharpe and Harper, 2002). Hog slurry contains high amounts of inorganic N and easily degradable C, and when applied to soils it creates anaerobic conditions thus enhancing N<sub>2</sub>O emissions through denitrification (Granli and Bøckman, 1994; Sharpe and Harper, 2002; Velthof et al., 2003). The small increase in N<sub>2</sub>O fluxes towards the end of the incubation period, in this study may be partly attributed to the release of N due to mineralisation of organic N from applied slurry.

The addition of DCD to the slurry made no difference to the magnitude or the duration of the  $N_2O$  fluxes (Figure 4.1). Soil pH, however, affected  $N_2O$  fluxes (p<0.05) on all days except 7 and 18, while WFPS only affected  $N_2O$  fluxes (p<0.05) on days 1 and 2 (Table 4.3). A significant (p<0.05) pH×soil water interaction occurred at d 1, 2, and 14 (Table 4.3). A maximum flux (1050  $\mu$ g kg<sup>-1</sup> soil d<sup>-1</sup>) occurred at d 1 as a result of the interaction between the lowest soil pH (4.7) and the highest soil water content (90% WFPS). The implication of this is that, during the spring and fall in Atlantic Canada, when soils are generally excessively wet a substantial amount of  $N_2O$  may be emitted, particularly in soils with pH < 6.3.

# 4.3.2.2 Cumulative N<sub>2</sub>O Production

## 4.3.2.2.1 Effect of Amendment on Cumulative N<sub>2</sub>O Emissions

The addition of DCD to slurry had no significant (p>0.05) effect on cumulative  $N_2O$  emissions with an average 242 g  $N_2O$ -N ha<sup>-1</sup> (0.07% of applied N) lost (Table 4.2). Other studies have reported  $N_2O$ -N losses ranging from 0.05 to 3.3% (Chadwick et al., 2000; Flessa and Beese, 2000; Hatch et al., 2005; Malla et al., 2005). According to Bouwman (1990), between 0.01 and 2% of total N applied as organic fertiliser is lost as  $N_2O$ . The lower losses (i.e. %N applied) in the current study may be due to the shorter duration of the study (21 days). Bouwman (1990) reported results from studies that monitored  $N_2O$  emissions for at least one full growing season or a year.

Results of this study agree with Williamson and Jarvis (1997) who found no differences in N<sub>2</sub>O emissions when DCD was added to dung and stored wastewater. Similarly, Merino et al. (2001) found no differences on N<sub>2</sub>O emissions when DCD was added to slurry. Di and Cameron (2002) and Merino et al (2002) however, found that DCD reduced N<sub>2</sub>O emissions when added to cattle urine and cattle slurry, respectively. Hatch et al. (2005) reported similar results when mixing dairy slurry with DCD. The contrasting results confirm the observation that the effectiveness of DCD is dependent on soil and environmental factors such as temperature (Davies and Williams, 1995; Prasad and Power, 1995; Vallejo et al., 2001). Di and Cameron (2004), found that DCD degrades faster at air temperature of 20°C compared to 8°C, thus decreasing its inhibitory effect. The current study was conducted at 21°C, which might have increased the rate of DCD degradation, hence reducing its effectiveness.

The effectiveness of DCD might have also been masked by the initial low pH (4.7) of the soil used in this study. Generally, low soil pH inhibits nitrifying organisms, however, some studies have shown nitrification to take place in soils with pH< 4.5 (Granli and Bøckman, 1994; Bauhus et al. 1996; Dalal et al., 2003). This phenomenon has been attributed to existence of microsites with higher pH, occurrence of unknown nitrifiers and adaptation of autotrophic nitrifiers to acidic environments (Simek and Cooper, 2002). In addition, the high organic matter (6.5%) of the soil used in our study might have compromised the inhibitory effect of DCD. When soil organic matter is ≥5% the inhibitory effect of NIs ceases, and this is probably due to the effect of organic matter on sorption and the rate of decomposition of NIs (Prasad and Power,1995). The contrasting results may also mean that the effectiveness of DCD will also be affected by the type and characteristics of the slurry; i.e. hog slurry vs cattle slurry. Nonetheless, results of the present study suggest that the addition of DCD together with hog slurry is not effective in reducing N<sub>2</sub>O emissions from the Marshland (Acadia) soil.

## 4.3.2.2.2 Effect of Soil Water Content on Cumulative N2O Emissions

Soil water content had a significant (p< 0.05) effect on cumulative  $N_2O$  emissions (Table 4.2). The lowest water content (50% WFPS) resulted in significantly lower  $N_2O$  emissions compared to the other two soil water contents (70 and 90 %WFPS). There was a significant (p< 0.05,  $R^2$  =0.99) linear increase in  $N_2O$  emissions as soil water content increased from 50 to 90% WFPS (data not shown). Clough et al. (2004) reported that  $N_2O$  emissions increased exponentially as soil water content increased from 54 to 80% WFPS.

This finding is consistent with previous observations that as soil water content increases so do  $N_2O$  emissions (Clough et al., 2004; Dobbie and Smith, 2001; Maag and Vinther 1999). The fact that at 70 and 90% WFPS the  $N_2O$  emissions were not different confirms that the threshold for maximum  $N_2O$  production appears to be  $\geq 60\%$  WFPS. The pH×water content interaction had a significant (p< 0.05) effect on cumulative  $N_2O$  emissions. The highest cumulative  $N_2O$  losses were associated with the interaction between the lowest soil pH (4.7) and highest soil water content (90% WFPS).

# 4.3.2.2.3 Effect of Lime (pH) on Cumulative N<sub>2</sub>O Emissions

Cumulative  $N_2O$  emissions were significantly (p<0.05) affected by liming (Table 4.2). The highest cumulative  $N_2O$  emissions (547 g  $N_2O$ -N ha<sup>-1</sup>) were associated with the lowest soil pH (4.7). This accounted for 0.17% of total N applied, confirming previous observations that as soil pH decreases more  $N_2O$  is emitted (Nagele and Conrad, 1990; Weier and Gilliam, 1986). Weier and Gilliam (1986) observed that  $N_2O$  production ceased completely at soil pH > 5.8, but at pH of 5.7 and 4.2,  $N_2O$  emissions ranged from 2.0 to 21.7 mg  $N_2O$  kg<sup>-1</sup> soil, accounting for 15.1 to 92.5% of  $NO_3$ -N lost. As soil pH declines the reduction of  $N_2O$  is inhibited more than the reduction of  $NO_3$ -, and thus  $N_2O$  production becomes more dominant at soil pH < 5.5 (Dalal et al., 2003). This is what may have caused the higher  $N_2O$  emissions at the lowest soil pH in our study. Meanwhile, the lowest cumulative  $N_2O$  loss (46 g  $N_2O$ -N ha<sup>-1</sup>) representing 0.01% of total N applied was achieved with the intermediate soil pH (6.3). This loss however, was not significantly (p> 0.05) different from that achieved with liming the soil to pH 7.4, which amounted to 134 g  $N_2O$ -N ha<sup>-1</sup>, accounting for 0.04% of N applied.

Results of the present study confirm previous observations that liming soil to pH around 6.5 reduces N<sub>2</sub>O emissions. However, this decrease in N<sub>2</sub>O emissions with liming is accompanied by a significant increase in NH<sub>3</sub> volatilisation. The loss of N through NH<sub>3</sub> volatilisation reduces the inorganic-N pool available for nitrification and denitrification. Therefore, the decrease in N<sub>2</sub>O emission as the soil pH increased may partly be explained by the reduction of the inorganic-N pool (Clough et al., 2003). Findings of this study therefore, suggest that since most soils in Nova Scotia are generally acidic, they may potentially produce more N<sub>2</sub>O. However, if limed, more N will be lost through NH<sub>3</sub> volatilisation, creating a tradeoff between the two gases. Generally, the amount of NH<sub>3</sub> lost can be much larger than N<sub>2</sub>O, but N<sub>2</sub>O has a significant global warming potential (IPCC 1996b). On the other hand, NH<sub>3</sub> besides contributing to eutrophication and acidification of ecosystems, is known to take part in N<sub>2</sub>O formation. The IPCC (1996a) estimates that for every kg of NH<sub>3</sub>-N volatilised 0.01 kg of N<sub>2</sub>O-N is formed, while Ferm (1998) estimates that about 5% of the global N<sub>2</sub>O emissions are due to NH<sub>3</sub> oxidation.

### 4.4 CONCLUSIONS

This study has demonstrated that mixing DCD with hog slurry may not be effective in reducing  $N_2O$  emissions from Acadia soils. The amount of  $NH_3$  and  $N_2O$  lost increased with increasing soil water content, implying that emissions of these gases can be reduced by avoiding slurry application to excessively wet soils. Meanwhile, liming soil to  $pH \ge 6.3$  lowered  $N_2O$  emissions, while simultaneously increasing  $NH_3$  volatilisation. To better understand the interaction between  $NH_3$  and  $N_2O$ , and develop management strategies to

mitigate these gases, whole system studies are necessary. Most importantly though, gaseous N losses, can in general be reduced by using recommended N rates and proper slurry or manure application timing.

**Table 4.1.** Chemical and physical characteristics of the soil (0-20 cm depth) and hog slurry used in the study.

Characteristic	Soil	Hog Slurry
pH	4.71#	6.02
TN (%) <sup>a</sup>	0.33	0.28
Organic Carbon (%) <sup>a</sup>	3.80	1.20
C:N ratio	11.5	4.29
NH <sub>4</sub> (%)	nd	0.19
NO <sub>3</sub> (mg kg <sup>-1</sup> )	2.23	nd
DM (%)	na	3.13
Porosity (%)	58.5	na
Bulk Density (Mg m <sup>-3</sup> )	1.10	na
Organic Matter (%)	6.50	na
CEC (meq/100g)	14.1	na

nd = not determined, na = not applicable, \*pH 1:2 dry soil: deionised water, \*determined using CNS analyser.

Table 4.2. Effect of amendment, lime and soil water content (%WFPS) on  $NH_3$  volatilisation and cumulative  $N_2O$  emissions from an acidic Acadia soil over a 21-d measurement period.

Treatment		NH <sub>3</sub> -N loss (kg ha <sup>-1</sup> )	N <sub>2</sub> O-N loss (g ha <sup>-1</sup> )
Amendment	S	1.10 a	207.54 a
	S+DCD	1.09 a	277.15 a
Lime	pH 4.7	0.36 c	546.55 a
	pH 6.3	0.99 b	46.21 b
	pH 7.4	1.92 a	134.26 b
WFPS	50%	0.92 b	122.82 b
	70%	0.98 b	251.40 a
	90%	1.38 a	352.80 a

Means followed by the same letter within the same column and each treatment are not significantly different (p > 0.05) using DMRT.

**Table 4.3.** Summary of the analysis of variance (ANOVA) for the effects of soil pH, soil water content (%WFPS) and amendment (Amend) on daily  $N_2O$  fluxes during selected days.

Source of	P values					
variation	Day 1	Day 2	Day 3	Day 5	Day 14	Day 21
pН	0.001**	0.001**	0.001**	0.026*	0.028*	0.009**
WFPS	0.001**	0.002**	0.165	0.776	0.134	0.309
Amend	0.539	0.172	0.383	0.47	0.333	0.324
pH×WFPS	0.001**	0.004**	0.103	0.706	0.043	0.547
pH×Amend	0.188	0.559	0.478	0.305	0.67	0.352
WFPS×Amend	0.658	0.69	0.903	0.418	0.403	0.713
pH×WFPS×Amend	0.231	0.279	0.932	0.626	0.258	0.011*

<sup>\*,\*\*</sup> Significant at p < 0.05 and p < 0.01, respectively.

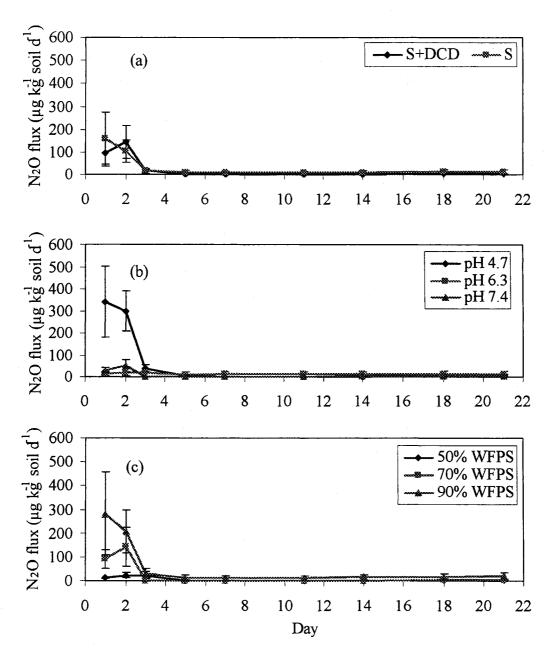


Figure 4.1. Mean daily  $N_2O$  evolution as impacted by (a) slurry (S) and slurry+DCD (S+DCD), (b) soil pH and (c) soil water content (WFPS) over a 21-d measurement period. Vertical bars represent standard error of mean (n = 3) (note, some error bars are smaller than symbols).

# **CHAPTER 5**

The Impact of Management Practices and Meteorological Conditions on Ammonia and Nitrous Oxide Emissions Following Application of Hog Slurry to Acidic Soils

#### **ABSTRACT**

Nitrogen (N) loss from field applied slurry through ammonia (NH<sub>3</sub>) volatilisation has led to the adoption of nutrient management strategies. While, several options have been effective, concern is growing that some may simultaneously enhance nitrous oxide (N<sub>2</sub>O) emissions, thus negating their overall benefits. This field study evaluated the impact of slurry application rate, soil water status, slurry dilution, simulated rainfall and meteorological conditions on NH<sub>3</sub> and N<sub>2</sub>O emissions following hog slurry application on acidic soils (pH< 6.5) seeded to grass. Increasing the application rate increased NH<sub>3</sub> losses. Applying slurry to plots that received water prior to application increased NH<sub>3</sub> losses by 8%, compared to the plots that did not receive water. Diluting slurry decreased NH<sub>3</sub> losses by 41%, while rainfall (~6mm) after slurry application reduced NH<sub>3</sub> emissions by 45%. Ammonia losses increased with higher air and soil temperatures, net radiation, vapour pressure deficit, and evapotranspiration. These management strategies and the various meteorological conditions had no effect on N<sub>2</sub>O emissions, presumably due to low soil NO<sub>3</sub>-N contents in these soils. Therefore, NH<sub>3</sub> losses can be reduced without increasing N<sub>2</sub>O losses by diluting slurry, applying slurry before forecasted rainfall, and most importantly applying slurry during cool days with reduced evaporative demand. Since estimated indirect N<sub>2</sub>O emissions (i.e. emissions due to volatilised NH<sub>3</sub>) were higher than direct emissions, more effort should be directed towards reducing NH<sub>3</sub> losses.

#### **5.1 INTRODUCTION**

Ammonia (NH<sub>3</sub>) volatilisation is a major pathway for gaseous nitrogen (N) loss from field applied manure. It is estimated that up to 65% of the NH<sub>3</sub> can be lost within 10 h of manure application (Gordon et al., 2001). Ammonia is an important atmospheric pollutant, which contributes to eutrophication and acidification of ecosystems (FAO, 2001; Rotz, 2004), and also in the formation of nitrous oxide (N<sub>2</sub>O), a potent greenhouse gas (IPCC, 1996b; Ferm, 1998).

Ammonia loss is governed by several processes including the difference in partial pressure between the manure surface and atmosphere, meteorological conditions, manure and soil characteristics, and management practices/strategies (FAO, 2001; Rotz, 2004). Meteorological conditions which affect NH<sub>3</sub> loss include air and soil temperature, solar radiation, windspeed, vapour pressure deficit (VPD) and rainfall (Beauchamp et al., 1982; Brunke et al., 1988; Gordon et al., 2001; Moal et al., 1995). Losses can therefore, be minimised by scheduling manure spreading activities based on the weather forecast. Among manure characteristics, dry matter (DM) content, total ammoniacal nitrogen (TAN) and pH are the most important (Rotz, 2004). Ammonia losses generally increase with an increase in manure DM, TAN and pH (Rotz, 2004; Sogaard et al., 2002; Sommer and Hutchings, 2001).

Management practices which can reduce NH<sub>3</sub> volatilisation from land applied manure include application rate, manure dilution, manure acidification, incorporation immediately after or injection and rainfall shortly after spreading (Malgeryd, 1998; Rotz, 2004). Application rate and slurry DM content can be manipulated to reduce losses. Reduced N losses are likely to occur with a single heavy application than with several lighter applications

that provide the same total applied N (Rotz, 2004). Manure dilution reduces the manure NH<sub>4</sub><sup>+</sup>-N concentration and DM content and improves manure soil infiltration, thus decreasing volatilisation (Sommer and Hutchings, 2001).

Manure incorporation or injection reduces NH<sub>3</sub> volatilisation by up to 90% depending on the time of incorporation or the depth of injection (Dosch and Gutser, 1996; Thompson and Meisinger, 2002). Direct injection is the most effective method of reducing NH<sub>3</sub> losses (Rotz, 2004).

Heavy rainfall before manure application increases soil water content which may decrease manure infiltration, resulting in higher NH<sub>3</sub> losses. Moreover, heavy rain after manure application may result in nitrate-N (NO<sub>3</sub>-N) leaching and may also wash away the manure, thus negatively impacting adjacent water systems. Meanwhile, light rainfall or irrigation following spreading reduces NH<sub>3</sub> emissions. The water added delays the drying process, washes the manure off plants and transports the manure N into soil colloids (Malgeryd, 1998).

Although these management practices have demonstrated reduced NH<sub>3</sub> losses, there is a growing concern that some may increase N<sub>2</sub>O emissions, thus reducing their overall benefits. Nitrous oxide is produced in soils principally through nitrification and denitrification processes, which are controlled by N and C availability, oxygen supply, temperature and soil water content (Granli and Bøckman, 1994). Therefore, management practices that increase N and C availability, reduce oxygen supply or increase soil water content can potentially enhance N<sub>2</sub>O emissions. Establishing management strategies that reduce NH<sub>3</sub> losses without concomitantly increasing N<sub>2</sub>O emissions is essential and can only be achieved by

simultaneously assessing both. Such studies, however, are lacking.

The primary objective of this study was therefore to evaluate several adaptive management practices on NH<sub>3</sub> and N<sub>2</sub>O emissions following the surface application of hog slurry to acidic grassland soils. A secondary objective involved evaluating the impact of meteorological conditions on emissions, for the purpose of identifying the most appropriate conditions under which manure can be applied minimising both NH<sub>3</sub> and N<sub>2</sub>O losses. Management practices evaluated included: (i) slurry application rate, (ii) soil water status during slurry application, (iii) slurry dilution, and (iv) simulated rainfall soon after slurry application.

#### **5.2 MATERIALS AND METHODS**

# 5.2.1 Experimental Location, Site Description and Design

Several field experiments were conducted during the growing seasons (June to October) of 2003 through 2005 on three acidic soils seeded to forage grass in Great Village, Nova Scotia (45°25'N, 63°36'W). The forage grass was a mixture of timothy (*Phleum pratense*) and meadow fescue (*Festuca pratensis*). In 2003, the soil was an Acadia fine loam (Gleyed Regosol (AAFC, 1998a, Webb, et al., 1991). Acadia soils are strongly to slightly acid deep level silt loam to silty clay loam, marine sediments and have slow to extremely slow permeability. Acadia soils were reclaimed from salt marsh and dyked to protect them from tidal flooding. In 2004, the soil was a Truro fine sandy loam (Orthic Humo-Ferric Podzol) (AAFC, 1998a; Webb, et al., 1991). Truro soils have developed on fine sandy to coarse loamy glacio-fluvial sediments and are well drained. In 2005, the soil used was a Hebert

sandy-skeletal (Orthic Humo-Ferric Podzol) (AAFC, 1998a; Webb, et al., 1991). Hebert soils have developed on coarse loamy-gravel over sandy to sandy skeletal, glacio-fluvial sediments and are rapidly to well drained. Physical and chemical characteristics of the soils are shown in Table 5.1.

In 2003 and 2004 field experiments consisted of six circular plots, 7 m in diameter and separated by 3 m (Appendix 3). The plots were used for the measurement of NH<sub>3</sub> and N<sub>2</sub>O emissions as well as selected soil properties. In 2005, for NH<sub>3</sub> volatilisation measurements, experiments consisted of six rectangular plots (0.5 m × 2 m) separated by 3 m (Appendix 4). Next to each of these plots, additional plots measuring 2 m × 2 m with similar treatments were utilised for N<sub>2</sub>O emissions and selected soil properties measurements. In all years, plots were arranged in a straight line perpendicular to the direction of the prevailing wind to prevent cross contamination. Treatments during each experiment were assigned in a randomised complete block (RCB) design and replicated three times.

#### **5.2.2 Treatments**

Hog (Sus scrofa) manure slurry collected from a nearby commercial operation was used in all experiments and its characteristics are shown in Table 5.1. To obtain an even distribution, slurry was applied manually using buckets. Several experiments were conducted each year (June to October) comparing the impact of the following treatments on NH<sub>3</sub> and N<sub>2</sub>O emissions: (i) slurry application rate, (ii) soil water status at time of application, (iii) slurry dilution, and (iv) rainfall simulation immediately after slurry application.

The slurry application rate experiments involved a conventional (1x) rate (60,000 L

ha<sup>-1</sup>) versus either a 2x rate (120,000 L ha<sup>-1</sup>) or a 3x rate (180,000 L ha<sup>-1</sup>). Three randomly selected plots received hog slurry at 1x while the other three received either the 2x or 3x rate.

The soil water status experiments examined the effect of soil water content at the time of spreading on  $NH_3$  and  $N_2O$  emissions. Different soil water contents were achieved by applying water to three randomly selected plots prior to slurry application. The remaining three plots received no supplemental water. The amount of water applied ranged from 31 to  $220 L m^{-2}$  and these values are shown in Table 5.2 as rainfall equivalent (mm).

Dilution experiments evaluated the effect of slurry dilution on emissions. In 2003, slurry was diluted using 25% water (v/v). In 2004, the dilutions were either 50 or 100% (v/v), while in 2005, they were 100% (v/v). The dilutions were done in such a way that all plots received similar rates of N to eliminate variability due to different N rates.

The rainfall simulation experiments examined the impact of watering after slurry application on NH<sub>3</sub> and N<sub>2</sub>O emissions. Water (6 mm) was applied manually to three randomly selected plots immediately after slurry application, using watering cans with spouts. The other remaining three plots received no water. Treatments during each experiment were assigned in a randomised complete block (RCB) design and replicated three times. Details of the treatments examined and start dates of each experiment are provided in Table 5.2.

#### 5.2.3 Ammonia Volatilisation Measurements

In 2003 and 2004, NH<sub>3</sub> emissions were monitored using static chambers (traps) made from plexiglass (Appendix 2a). The traps measured 40 cm (height)  $\times$  20 cm  $\times$  20 cm placed randomly in plots soon (10 min) after manure spreading. The traps were inserted into the soil

to a depth of 1-2 cm to minimise NH<sub>3</sub> leakage between the soil and traps. Absorber foam measuring 20.5 cm × 20.5 cm × 2.5 cm was immersed in a glycerol-phosphoric acid solution prepared from 50 ml L<sup>-1</sup> glycerol and 50 ml L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> (Gordon et al, 2000; Kunelius et al., 1987). The foam absorbers were made to fit tightly to the traps to reduce NH<sub>3</sub> leakage between the trap and foam. Two foam absorbers per trap were used; one at the bottom (30 cm from the soil) trapped NH<sub>3</sub> volatilised from the soil and the upper one at the top of the chamber protected the bottom absorber from atmospheric NH<sub>3</sub>. The traps had a triangular plexiglass on top, which protected the absorbers from rainfall but allowed free air movement. After 6 h, 1, 2, 4, 7 and 10 d following slurry spreading, the foam absorbers were removed from the traps and placed in freezer bags, which were immediately sealed and subsequently put in large plastic bags. The top absorber was discarded while the bottom absorber was thoroughly rinsed in 250 mL 2M KCl to extract the trapped NH<sub>3</sub>. The solution was decanted into vials and kept frozen until analysis using a Technicon auto-analyser (Technicon Instruments, Tarrytown, NY) (Keeney and Nelson, 1982). Total NH<sub>3</sub> losses (kg N ha<sup>-1</sup>) were calculated on the basis of the soil surface area (0.04 m<sup>2</sup>) covered by the traps. The major advantages of the traps (chambers) are that they are cheap, simple to construct and can measure small fluxes, while the major disadvantage is that they alter the micrometeorological conditions i.e., temperature, windspeed, relative humidity and rainfall (FAO, 2001).

In 2005, NH<sub>3</sub> emissions were measured using six wind tunnels similar in design and size to Chantigny et al. (2004a) and Rochette et al. (2001) (Appendix 4). The tunnels consisted of an inverted U-shaped cover made out of transparent acrylic plastic pinned along each edge of a metal frame covering 1 m<sup>2</sup> (0.5 m  $\times$  2 m). The canopy section was connected

to a circular steel duct housing a fan. Air speed within each tunnel was manually recorded several (4-5) times during each sampling period using a hand held hot-wire anemometer (Extech Instruments Corporation, Waltham, MA). Following slurry application, tunnels were immediately placed on the treated plots and measurements initiated within 5 min and continued for approximately 5 d. The tunnels were inserted into the soil to a depth of 5 cm to minimise NH<sub>3</sub> leakage between the soil and the tunnels. The air entering and leaving the tunnel was continuously sampled at 3 L min<sup>-1</sup> into volumetric flasks containing 100 mL of 0.005 M H<sub>3</sub>PO<sub>4</sub> acid using vacuum pumps (Thomas Pumps and Compressors, Sheboygan, WI). The pumps were connected to Gallus 2000 gas flow meters (Actaris Metering Systems, Greenwood, SC) housed in an adjacent trailer. At the end of each sampling period, the used acid solution was replaced with new acid solution. The acid solution was replaced three times daily during the first and second day of the experiment and thereafter twice daily for the next 3 d. The used acid solution was then made up to 100 mL with  $0.005 \text{ M H}_3PO_4$  and kept frozen until analysis for NH<sub>4</sub><sup>+</sup>-N using a Technicon auto-analyser (Technicon Instruments, Tarrytown, NY) (Keeney and Nelson, 1982). The detection limit for NH<sub>4</sub><sup>+</sup>-N was 0.03 mg L<sup>-1</sup>. The NH<sub>3</sub> flux was calculated as follows:

$$F_{NH3} = \frac{f}{A} (C_{out} - C_{in}) \tag{1}$$

where  $F_{NH3}$  is the ammonia flux (kg N h<sup>-1</sup> d<sup>-1</sup>), f is the total volume of air flowing through the tunnel (L h<sup>-1</sup>), A is the enclosed surface area (1 m<sup>2</sup>),  $C_{in}$  and  $C_{out}$  are the NH<sub>3</sub> concentration (mg N L<sup>-1</sup>) of air entering and leaving the tunnel, respectively.

#### 5.2.4 Nitrous Oxide Emissions Measurements

Emissions of N<sub>2</sub>O were measured using vented static chambers (Appendix 2b). The chambers were made out of polyvinyl chloride (PVC) and consisted of a collar (bottom) and a top (chamber). The collars measured 20 cm inside diameter × 10 cm height while the chambers measured 20 cm inside diameter × 15 cm height. The chambers were insulated with foam plastic lined with aluminium foil to minimise temperature increase inside the chamber during sampling. Soon (30 min) after slurry application, one collar plot-1 was inserted to the soil to a depth of about 5 cm and left open to the atmosphere throughout the duration of each experiment. During sampling, chambers were attached to the collars and 20 mL gas samples were collected through a rubber septum at regular intervals (0, 10, 20 and 30 min) using plastic disposable syringes (Becton-Dickinson, Franklin Lakes, NJ) and subsequently transferred to 12 mL pre-evacuated vials (Labco Exetainer, High Wycombe, UK) which were sealed with silicone to prevent gas leakage and kept until analysis. Prior to gas sampling, head-space gas was thoroughly mixed by pumping several times with the syringe. Gas samples were collected once a day for 2-3 d starting immediately (30 min) after application of treatments, and thereafter at an increasing interval for a maximum of 21 d. Nitrous oxide concentrations were analysed using a Varian GP3800 gas chromatograph (GC) fitted with an electron detector (Varian Inc., Palo Alto, CA). The rate of N<sub>2</sub>O emission (flux) was calculated assuming a linear increase in gas concentration (Hutchinson and Livingston, 1993):

$$F_{N2O} = \frac{dC}{dT} x \frac{V}{A} x \frac{M}{V_{mol}}$$
 (2)

where  $F_{N2O}$  is the rate of  $N_2O$  flux (µg of  $N_2O$  m<sup>-2</sup> min<sup>-1</sup>), dC/dT is the rate of change of  $N_2O$  concentration within the chamber (µmol mol<sup>-1</sup> min<sup>-1</sup>), V is the chamber head-space volume (m<sup>3</sup>), A is the bottom surface area of the chamber (0.031 m<sup>2</sup>), M is the molecular weight of  $N_2O$  (44 g mol<sup>-1</sup>) and  $V_{mol}$  is the volume of a mole of gas at 20 °C (0.024 m<sup>3</sup> mol<sup>-1</sup>).

# 5.2.5 Soil Sampling and Analysis

Soil samples for NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N analysis were collected 3-4 times during each experiment. During each soil sampling period, three samples per plot (0-15 cm depth) were collected from each plot and mixed to make a composite sample using a hand-held auger and placed in pre-labeled soil sample bags. Samples were air-dried and passed through a 2 mm sieve. Subsamples of 5 g were shaken with 50 mL of 2 M KCl for 45 min and the soil suspensions were filtered through Whatman number 42 filter papers. Filtrates were kept frozen until analysis for NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N using a Technicon auto-analyser (Technicon Instruments, Tarrytown, NY) (Keeney and Nelson, 1982). The detection limits for NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N were 0.03 and 0.05 mg L<sup>-1</sup>, respectively.

## 5.2.6 Meteorological Measurements

From each plot, soil temperature at 10 cm depth was recorded using copper-constantan thermocouples and volumetric soil water content ( $\theta_v$ ) at 0-20 cm depth was measured using time domain reflectometry (TDR). In 2003, soil moisture probes were ECH<sub>2</sub>O Dielectric Aquameter (Decagon Devices Inc., Pullman, WA), while in 2004 and 2005 they were Campbell CS615 (Campbell Scientific Corp., Logan, UT). Additionally, rainfall

(tipping bucket rain gauge), windspeed and direction (anemometer and wind vane), net radiation (net radiometer), soil heat flux (heat flux plates), relative humidity and vapour pressure deficit (relative humidity and temperature probe), air and soil temperature (thermocouples) were also recorded utilising a Bowen Ratio Energy Balance (BREB) system (Radiation and Energy Balance System Inc, Seattle, WA) (Appendix 8). Evapotranspiration (ET) rates (mm d<sup>-1</sup>) were calculated using latent heat data computed from the BREB (Oke, 1996; Peacock and Hess, 2004). All data were recorded at 60 s intervals and averaged over 15 min using a CR10X data-logger (Campbell Scientific Corp., Logan, UT).

## 5.2.7 Statistical Analysis

Data from each experiment were subjected to analysis of variance (ANOVA) using the PROC GLM function of SAS (SAS Institute, 1996). For both N<sub>2</sub>O and soil inorganic N, data for each sampling day were analysed separately. Differences among treatments were declared to be significant at p< 0.05. Cumulative N<sub>2</sub>O losses were calculated by integrating N<sub>2</sub>O losses measured between sampling periods. Due to high variability and violation of the normality and constant variance assumptions, N<sub>2</sub>O data were log-transformed before analysis. Correlation and regression analysis were performed to relate gas emissions to average meteorological conditions. In 2003 and 2004, NH<sub>3</sub> fluxes (kg N ha<sup>-1</sup> d<sup>-1</sup>) in the 24 h following slurry application for similar experiments were pooled and used to establish the relationship with meteorological variables, while in 2005, NH<sub>3</sub> fluxes in the 20 h following slurry application were used. The slightly different approaches were warranted by the different methods used to measure NH<sub>3</sub> losses, as described in the materials and methods section. In

all years, daily N<sub>2</sub>O fluxes were used to establish the relationship between N<sub>2</sub>O fluxes and meteorological variables. Indirect N<sub>2</sub>O emissions were estimated according to (IPCC, 1996a); for every kg of NH<sub>3</sub>-N volatilised 0.01 kg of N<sub>2</sub>O-N is formed.

#### 5.3 RESULTS AND DISCUSSION

#### 5.3.1 Ammonia Losses

# 5.3.1.1 Slurry Application Rate

The 2x and 3x slurry application rates resulted in higher total NH<sub>3</sub> losses (p<0.05) on 5 of the 8 experiments (Table 5.3). Losses ranged from 3 to 30 kg N ha<sup>-1</sup> for the 1x rate, 6 to 50 kg N ha<sup>-1</sup> for the 2x rate and 3 to 50 kg N ha<sup>-1</sup> for the 3x rate. Total NH<sub>3</sub> losses as a percentage (%) of applied NH<sub>4</sub><sup>+</sup>-N ranged from 2 to 28%, 2 to 17% and 1 to 25% for the 1x, 2x and 3x rates, respectively. Using wind tunnels, Moal et al (1995) recorded total NH<sub>3</sub> losses ranging from 5 to 63% of pig slurry NH<sub>4</sub><sup>+</sup>-N applied to grassland, while Thompson and Meisinger (2002) recorded losses equivalent to 40% and 28% of cattle slurry NH<sub>4</sub><sup>+</sup>-N applied to grass and bare soil, respectively. Likewise, Chantigny et al. (2004a) recorded NH<sub>3</sub> losses equivalent to 45% of pig slurry NH<sub>4</sub><sup>+</sup>-N applied, over 19 d. The lower NH<sub>3</sub> losses in the current study were presumably caused by the lower soil and slurry pH (Table 5.1), as well as different climatic conditions and durations of measurements.

In all but one experiment, the total NH<sub>3</sub> losses expressed as % of applied slurry NH<sub>4</sub><sup>+</sup>-N decreased with increasing slurry application rate. Sognard et al. (2002) found that NH<sub>3</sub> volatilisation expressed as a fraction of total ammoniacal nitrogen (TAN) applied, decreased when the slurry application rate increased. This is presumably due to a greater proportion of

the slurry infiltrating into the soil and also drying (crusting) of the slurry (Sommer and Hutchings, 2001). After drying, slurry dry matter may form a crust, which acts as a diffusion barrier between the soil and atmosphere, reducing NH<sub>3</sub> volatilisation (Sommer et al., 2003).

### 5.3.1.2 Soil Water Status

Soil water status at the time of slurry spreading had no effect (p> 0.05) on NH<sub>3</sub> emissions, with losses ranging from approximately 10 to 39 kg N ha<sup>-1</sup> for the plots that received water prior to application and 10 to 29 kg N ha<sup>-1</sup> for the plots that did not receive water (Table 5.4). Total NH<sub>3</sub> losses expressed as a % of applied slurry NH<sub>4</sub><sup>+</sup>-N ranged from approximately 4 to 43% for the plots that received water and from 4 to 42% for the plots that did not receive water. These results somewhat contradict previous observations, which showed that higher initial soil water increased NH<sub>3</sub> losses (Sogaard et al., 2002; Sommer, 2001). This was presumably caused by the fact that the  $\theta_{\nu}$  for plots that received water prior to application were not much different from those of plots that did not receive water (Table 5.4). Significant amounts of the applied water were lost through runoff and high infiltration rates, particularly with the Truro and Hebert soils. In 2003, the average  $\theta_v$  during the 10 d NH<sub>3</sub> measurement period was, 29 and 32% for the plots that did not receive water and the plots that received water prior to application, respectively. In 2004,  $\theta$ , was 29 and 31% for the plots that received water prior to application and the plots that did not receive water, respectively. In 2005 meanwhile,  $\theta_v$  ranged from 13 to 29% for the plots that received water prior to application and 23 to 33% for the plots that did not receive water. Genermont and Cillier (1997) showed that high  $\theta_{v}$  at the time of slurry application can increase NH<sub>3</sub>

volatilisation. They attributed this to reduced infiltration of the slurry due to high  $\theta_v$ .

Although the total NH<sub>3</sub> losses were not different (p> 0.05) between treatments, there was, however, a trend showing an increase in NH<sub>3</sub> losses with plots that received water prior to slurry application. The increase in NH<sub>3</sub> losses as a result of the wetter soil conditions ranged from 0 to 25% with an average of 8% difference. This is close to the 10% increase in losses predicted by Sogaard et al. (2002) for animal slurry applied to a wet soil compared to a dry soil. Their study, however, did not clearly define wet and dry. This result implies that even small increases in  $\theta_v$  may potentially increase NH<sub>3</sub> losses; thus losses can be possibly reduced by avoiding applying slurry to wet soils.

## 5.3.1.3 Slurry Dilution with Water

Slurry dilution with water generally decreased NH<sub>3</sub> losses, however, losses were different (p<0.05) in 3 of the 6 experiments (Table 5.5). Total NH<sub>3</sub> losses ranged from 2 to 23 kg N ha<sup>-1</sup> for diluted slurry and 4 to 23 kg N ha<sup>-1</sup> for undiluted slurry. When expressed as a % of applied NH<sub>4</sub><sup>+</sup>-N, losses for diluted slurry ranged from 2 to 35%, while those for undiluted slurry ranged from 3 to 35%. Compared to undiluted slurry, dilution reduced total average NH<sub>3</sub> losses by 41% when the dilution was 100% (1:1), 31% when the dilution was 50% (1:0.5) and 20% when the dilution was 25% (1:0.25). Stevens et al. (1992) reported that dilution of cattle slurry by 100% reduced NH<sub>3</sub> loss by 50% compared to undiluted slurry. Genermont and Cellier (1997) using a model predicted that diluting slurry by 100% would reduce NH<sub>3</sub> loss by 54% compared to undiluted slurry.

Total NH<sub>3</sub> loss was negatively correlated ( $R^2 = 0.96$ , p < 0.1) with slurry dilution (data

not shown). Brunke et al. (1988) found a similar relationship between NH<sub>3</sub> flux density and swine manure dilution, when using dilutions of 25, 50, 75 and 100%. Frost (1994) also found that NH<sub>3</sub> losses decreased linearly when beef manure was diluted with 0, 50, 100 and 150% water before field-application. Moal et al. (1995) observed a positive linear relationship (R<sup>2</sup> = 0.78) between NH<sub>3</sub> loss and slurry DM content. Dilution with water decreases the slurry DM content and viscosity, thus improving slurry infiltration into the soil, which in turn reduces NH<sub>3</sub> volatilisation. In the current study, on average dilution decreased the slurry dry matter content from 4.4% to 2.2%. This implies that NH<sub>3</sub> losses can be reduced by diluting manure before field-application. The major drawback to this strategy, however, is the increased volume of manure to be handled.

# 5.3.1.4 Rainfall After Slurry Application

Simulated rainfall after slurry application reduced (p<0.05) total NH<sub>3</sub> losses (Table 5.6). Total NH<sub>3</sub> losses ranged from approximately 3 to 10 kg N ha<sup>-1</sup> for the simulated rainfall treatment and 5 to 14 kg N ha<sup>-1</sup> for the no-rainfall treatment. Losses as a % of NH<sub>4</sub><sup>+</sup>-N applied ranged from 2 to 16% and 4 to 28% for the simulated rainfall and no-rainfall treatments, respectively. Ammonia loss reduction due to simulated rainfall ranged from 25 to 63%, with an average of 45%. This result is in agreement with previous studies which showed that rainfall or irrigation soon after slurry application reduces volatilisation. Sommer and Hutchings (2001) found that 20 mm of irrigation after spreading pig manure reduced NH<sub>3</sub> losses by 50% compared to unirrigated treatments. Genermont and Cellier (1997) using a model, estimated that a 20 mm irrigation soon after slurry application reduced losses by

48%. Likewise, Malgeryd (1998) reported that a 30 mm irrigation immediately after spreading pig slurry reduced losses by 70%. Gordon and Schuepp (1994) found slightly lower NH<sub>3</sub> losses from plots that were watered daily with 4 to 8 mm after manure application, however, the difference was not significant. Rainfall soon after slurry application increases the rate of slurry infiltration into the soil, dilutes the slurry TAN concentration, decreases evapotranspiration and lowers surface temperature, hence reducing volatilisation. The implication of this result is that, NH<sub>3</sub> losses can be reduced by applying slurry before possible rainfall or use of irrigation immediately after slurry application.

#### 5.3.2 Nitrous Oxide Emissions

In all three years of the study, daily N<sub>2</sub>O fluxes were not affected (p> 0.05) by slurry application rate, soil water status, slurry dilution and simulated rainfall. Regardless of treatments, fluxes were generally low (~ 5 g N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup>) and often negative, even with the highest slurry application rates (data not shown). The low fluxes were unexpected since pig slurry has been shown to enhance N<sub>2</sub>O emissions, particularly soon after application. For example, Chadwick et al. (2000) recorded N<sub>2</sub>O fluxes as high as 264 g N ha<sup>-1</sup> d<sup>-1</sup> after applying pig slurry to grassland in England. The low fluxes in the present study were presumably caused by low soil NO<sub>3</sub><sup>-</sup>-N contents due to slow nitrification of the slurry NH<sub>4</sub><sup>+</sup>-N (Mkhabela et al., 2007). Most of the inorganic N in the slurry was in the NH<sub>4</sub><sup>+</sup> form (52 to 71% of total N), which had to be converted to NO<sub>3</sub><sup>-</sup> by nitrifying organisms before being denitrified to N<sub>2</sub>O and/ or N<sub>2</sub>. For most experiments, soil NO<sub>3</sub><sup>-</sup>-N contents were generally < 5 mg kg<sup>-1</sup> during all soil sampling occasions, while soil NH<sub>4</sub><sup>+</sup>-N contents were generally >

30 mg kg<sup>-1</sup> (Table 5.7). When soil nitrate is low, N<sub>2</sub>O fluxes will be low even when all other conditions are optimal (Dobbie and Smith, 2003). A soil NO<sub>3</sub><sup>-</sup>-N content of 5 mg kg<sup>-1</sup> is generally regarded as the minimum threshold for N<sub>2</sub>O production (Granli and Bøckman, 1994; Whalen, 2000). Sherlock et al. (2002) also recorded low N<sub>2</sub>O fluxes (1 g N ha<sup>-1</sup> h<sup>-1</sup>) in the first 14 d after pig slurry application and attributed this to low soil NO<sub>3</sub><sup>-</sup>-N (< 5 mg kg<sup>-1</sup>). They further reported that after the first 14 d, fluxes increased to a maximum of 7.5 g N ha<sup>-1</sup> h<sup>-1</sup> and this increase coincided with an increase in soil NO<sub>3</sub><sup>-</sup>-N contents (>5 mg kg<sup>-1</sup>).

Similar to  $N_2O$  fluxes, cumulative  $N_2O$  losses were generally not affected (p> 0.05) by all the treatments during the three years of the study (Tables 5.3 to 5.6). Overall cumulative  $N_2O$  losses ranged from 9 to 1800 g N ha<sup>-1</sup>. When expressed as % of total slurry N applied (uncorrected for background emissions), losses accounted for 0.003 to 0.72 %, giving an overall average of 0.13%. These losses are lower than those recorded by other authors using hog or dairy slurries. Over a 90 d measurement period, Sherlock et al. (2002) recorded total  $N_2O$  losses equivalent to 2.1% of applied N after spreading pig slurry to a New Zealand pasture. In experiments that lasted 8 or 11 d, Whalen (2000) recorded  $N_2O$  losses ranging from 0.05 to 1.0% of total N applied as liquid swine waste or inorganic N. Chadwick et al. (2000) recorded cumulative  $N_2O$  losses ranging from 0.12 to 0.97% of total N applied as pig or dairy slurries during experiments that lasted 24 d. Results of the current study therefore, imply that hog slurry when applied to acidic grassland soils (pH < 6.5) has no major impact on  $N_2O$  emissions, even when applied at extremely high rates. It has to be emphasised, however, that the  $N_2O$  emissions recorded in the current study were of short duration (maximum 21 d) and therefore can not be used to estimate annual emissions. The aim of this

short-term study was to compare different treatments and not to determine annual emissions.

## 5.3.3 Impact of Meteorological Variables on Gas Emissions

## 5.3.3.1 Ammonia Volatilisation

Figures 5.1 and 5.2 and Table 5.8 show the relationship between NH<sub>3</sub> emissions and several meteorological variables in 2004 and 2005. Regardless of NH<sub>3</sub> measurement method, the relative influence of meteorological conditions on NH<sub>3</sub> loss was similar. For unknown reasons, the relationship in 2003 was poor and therefore was omitted. Except for soil temperature in 2003, all selected meteorological variables correlated significantly (p< 0.05) with NH<sub>3</sub> flux in both years, confirming that meteorological conditions play a major role in NH<sub>3</sub> loss. In 2004, the R<sup>2</sup> ranged from 0.30 to 0.73, with soil temperature giving the lowest and evapotranspiration the highest. In 2005, the R<sup>2</sup> ranged from 0.48 to 0.69, with evapotranspiration yielding the lowest and net radiation the highest. The meteorological variables explained from 38 to 76% and 48 to 69% of the variation in NH<sub>3</sub> volatilisation in 2004 and 2005, respectively.

Results of the current study compare well with those reported by Brunke et al. (1988) in Quebec, who observed that  $NH_3$  flux density correlated significantly with windspeed, sensible heat, net radiation, soil heat, latent heat, air and surface temperatures. Gordon et al. (2001) found that  $NH_3$  loss in the 10 h following manure application positively correlated with solar radiation ( $R^2$ = 0.56), VPD ( $R^2$ = 0.53), windspeed ( $R^2$ = 0.53) and air temperature ( $R^2$ = 0.34). In France, Moal et al. (1995) reported good correlation between total  $NH_3$  loss and air temperature ( $R^2$ = 0.37) and soil temperature ( $R^2$ = 0.42). Results of the present study

support the conclusion by Gordon et al. (2001), that NH<sub>3</sub> loss from field-applied manure can be minimised by applying manure during cool days.

#### 5.3.3.2 Nitrous Oxide Flux

The relationship between  $N_2O$  flux and the recorded meteorological variables including soil water content (%WFPS) was poor (data not shown). This was presumably caused by the low soil  $NO_3^--N$  contents (< 5 mg kg<sup>-1</sup>). In Great Britain, Dobbie and Smith (2003) found that  $N_2O$  flux correlated significantly with %WFPS only when the soil  $NO_3^--N$  concentration was > 5 mg kg<sup>-1</sup> soil. Results of the current study therefore, suggest that meteorological conditions play a secondary role in  $N_2O$  emissions.

# 5.3.4 Tradeoff Between NH<sub>3</sub> and N<sub>2</sub>O

In this study, none of the NH<sub>3</sub> abatement strategies enhanced N<sub>2</sub>O emissions, mainly due to the low soil NO<sub>3</sub><sup>-</sup>-N. Total NH<sub>3</sub> losses, however, were much greater than N<sub>2</sub>O losses, but N<sub>2</sub>O has a significant global warming potential (IPCC, 1996b). On the other hand, NH<sub>3</sub> besides contributing to eutrophication and acidification of ecosystems, is known to take part in N<sub>2</sub>O formation. Ferm (1998) suggested that about 5% of the global N<sub>2</sub>O emissions are due to NH<sub>3</sub> oxidation. The IPCC (1996a) estimates that for every kg of NH<sub>3</sub>-N volatilised 0.01 kg of N<sub>2</sub>O-N is formed. Using this default emission factor, it is apparent that indirect N<sub>2</sub>O emissions (i.e., emissions due to volatilised NH<sub>3</sub>) were in the majority of cases much higher than direct (measured) emissions, ranging from 24 to 500 g N ha<sup>-1</sup> (Tables 5.3 to 5.6). Wulf et al. (2002) reported similar findings when studying the impact of application technique and

slurry co-fermentation on  $NH_3$  and greenhouse gas emissions. It should, however, be pointed out that the direct  $N_2O$  emissions reported in the current study were of short duration (maximum 21 d) and therefore may be an underestimation. Nevertheless, if this finding is correct, an important management implication is that, more emphasis should be directed towards reducing  $NH_3$  losses following application of hog slurry on these acidic soils. Long term studies are required to verify this finding. Another important observation emanating from this study is that strategies for mitigating these gases should consider many other factors such as soil type and pH and most importantly, local climatic conditions.

### **5.4 CONCLUSIONS**

Increasing slurry application rate increased NH<sub>3</sub> losses. Applying slurry to plots that received water before application increased NH<sub>3</sub> losses by 8% compared to plots that did not receive water. Slurry dilution decreased NH<sub>3</sub> losses by up to 57% relative to undiluted slurry. A 6 mm rainfall after slurry application reduced NH<sub>3</sub> emissions by an average of 45%. Due to low soil NO<sub>3</sub><sup>-</sup>-N contents, all management strategies evaluated in this study had no effect on N<sub>2</sub>O emissions. Regression analysis showed that, NH<sub>3</sub> losses increased with higher air and soil temperature, net radiation, evapotranspiration, and VPD. Thus, NH<sub>3</sub> volatilisation losses from field-applied hog slurry to acidic soils can be reduced without concomitantly increasing N<sub>2</sub>O emissions by (i) diluting slurry before application, (ii) applying slurry before possible light rainfall or irrigating soon after slurry application, (iii) applying slurry on dry soils, and (iv) applying slurry during cool days (low evaporative demand). Since estimated indirect N<sub>2</sub>O losses (i.e., losses due to volatilised NH<sub>3</sub>) were generally higher than direct losses, more

emphasis should be directed towards reducing  $\,\mathrm{NH_3}$  losses following application of hog slurry on these acidic soils.

Table 5.1. Chemical and physical characteristics of the soils (0-20 cm depth) and hog slurry

used in the study.

Characteristic	Acadia	Truro	Hebert	Slurry	Slurry	Slurry
	Soil	Soil	Soil	2003	2004	2005
pН	4.71#	6.05#	6.50#	6.22	5.81	5.55
TN (%)	0.33	nd	0.16	0.36	0.28	0.21
C (%)	3.80	nd	3.91	1.41	1.06	1.44
C:N ratio	11.5	nd	24.4	3.92	3.79	6.86
NH <sub>4</sub> <sup>+</sup> -N (%)	nd	nd	nd	0.24	0.20	0.11
NO <sub>3</sub> N (mg kg <sup>-1</sup> )	2.23	14.3	4.40	nd	nd	nd
Dry matter (%)	na	na	na	3.96	2.49	4.73
Porosity (%)	58.5	49.4	52.5			
Bulk Density (Mg m <sup>-3</sup> )	1.10	1.34	1.26			
Organic Matter (%)	6.50	5.05	4.10			
CEC (meq/100g)	14.1	11.3	10.6			

nd = not determined, na = not applicable, \*pH 1:2 dry soil: de-ionised water, TN and C determined using CNS analyser.

Table 5.2. Summary of experiments, start dates and treatments in 2003, 2004 and 2005.

Type of trial	Trial start date	Treatments compared#
Application rate	6 June 2003	60,000 vs. 120,000 L ha <sup>-1</sup>
	20 June 2003	60,000 vs. 120,000 L ha <sup>-1</sup>
	3 July 2003	60,000 vs. 180,000 L ha <sup>-1</sup>
	12 Sept 2003	60,000 vs. 120,000 L ha <sup>-1</sup>
	7 June 2004	60,000 vs. 120,000 L ha <sup>-1</sup>
	18 Oct 2004	60,000 vs. 180,000 L ha <sup>-1</sup>
	14 Sep 2005	60,000 vs. 180,000 L ha <sup>-1</sup>
	4 Oct 2005	60,000 vs. 180,000 L ha <sup>-1</sup>
Soil water status <sup>¶</sup>	22 July 2003	86 mm (wet) vs. No water
(water applied before slurry	28 July 2004	31 mm (wet) vs. No water
application)	23 June 2005	100 mm (wet) vs. No water
	8 July 2005	220 mm (wet) vs. No water
	27 July 2005	210 mm (wet) vs. No water
	19 Aug 2005	210 mm (wet) vs. No water
Slurry dilution	25 Aug 2003	25% water (volume)
	18 June 2004	50% water (volume)
	2 Sep 2004	100% water (volume)
	21 Sep 2004	100% water (volume)
	9 Aug 2005	100% water (volume)
	30 Aug 2005	100% water (volume)
Rainfall simulation <sup>¶</sup>	2 Sep 2004	6 mm water
(water applied after slurry	21 Sep 2004	6 mm water
application)	14 Sep 2005	6 mm water
	4 Oct 2005	6 mm water

<sup>&</sup>lt;sup>¶</sup>Values converted to equivalent rainfall (mm). <sup>#</sup>All experiments were replicated three times.

Table 5.3. Cumulative (total) ammonia (NH<sub>3</sub>) and nitrous oxide (N<sub>2</sub>O) losses as impacted by slurry application rate in 2003, 2004 and 2005.

Experiment	Slurry rate		Cumul	Cumulative gaseous N losses	N losses	
start date	(L ha <sup>-1</sup> )	NH <sub>3</sub> (kg N ha <sup>-1</sup> )	NH <sub>3</sub> loss (% NH <sub>4</sub> <sup>+</sup> -N applied)	$N_2O$ (g N ha <sup>-1</sup> )	$N_2O$ loss (% $N$ applied)	Indirect N <sub>2</sub> O losses (g N ha <sup>-1</sup> )¶
6 June 03	60,000	9.60 a 16.2 a	6.60 5.60	9.64 a 14.4 a	0.004	96*
20 June 03	60,000	6.80 b 21.1 a	4.70	150 a 119 a	0.07	68 211*
3 July 03	60,000	26.6 b 50.0 a	18.5	19.7 b 126 a	0.01	266*
12 Sept 03	60,000 120,000	29.9 b 49.9 a	20.8 17.3	9.30 a 14.5 a	0.04	299* 499*
7 June 04	60,000 120,000	5.90 a 5.50 a	4.90 2.30	1216 a 597 a	0.7	59 55
18 Oct 04	60,000	2.80 a 3.40 a	2.30	116 a 65.6 a	0.07	28
14 Sep 05	60,000	18.2 b 49.6 a	27.6 25.1	25.9 a 57.0 a	0.02	182* 496*
4 Oct 05	60,000 1 <b>8</b> 0,000	13.9 b 27.2 a	21.0 45.5 a 0.04 13.7 49.3 a 0.01	45.5 a 49.3 a	0.04	139* 272*

<sup>1</sup> Indirect N<sub>2</sub>O emissions estimated according to (IPCC, 1996a); for every kg of NH<sub>3</sub>-N volatilised 0.01 kg of N<sub>2</sub>O-N is formed. Means followed by different letters within the same column and each experiment are different at p< 0.05.

\* Indicates cases where indirect N2O losses due to volatilised NH3 are larger than direct (measured) emissions.

Table 5.4. Cumulative (total) ammonia (NH<sub>3</sub>) and nitrous oxide (N<sub>2</sub>O) losses as impacted by initial soil water status in 2003, 2004 and 2005. Volumetric water content  $(\theta_v)$  at the start of each experiment is also presented in the table.

Experiment	Treatments <sup>z</sup>	θ <sub>v</sub> at start		Cm	mulative gas	Cumulative gaseous N losses	
statt vate	applied)	experiment (%)	NH <sub>3</sub> (kg N ha <sup>-1</sup> )	NH <sub>3</sub> loss (% NH <sub>4</sub> <sup>+</sup> -N applied)	N <sub>2</sub> O (g N ha <sup>-1</sup> )	N <sub>2</sub> O loss (% N applied)	Indirect N <sub>2</sub> O losses (g N ha⁻¹)¶
22 July 2003	Water (86) No water (0)	36.8 30.5	39.0 a 29.2 a	13.5 10.1	1830 a 1580 a	0.42 0.37	390 292
28 July 2004	Water (31) No water (0)	38.4 33.5	9.9 a 9.9 a	4.1	711 a 1680 a	0.21	66
23 June 2005	Water (100) No water (0)	29.7 13.0	24.7 a 23.3 a	37.4 35.3	NR NR	1 1	247
8 July 2005	Water (220) No water (0)	27.4	22.5 a 21.2 a	34.1 32.2	356 a 145 a	0.28	225 212*
27 July 2005	Water (210) No water (0)	28.5 24.3	28.6 a 27.5 a	43.3	69 a 113 a	0.054	286* 275*
19 Aug 2005	Water (210) No water (0)	26.3 13.4	18.6 a 17.2 a	28.2 26.0	188 a 128 b	0.15	186 172*

<sup>2</sup> Numbers in brackets are the amount of water applied (mm) during each experiment, NR = Not Recorded. Means followed by different letters within the same column and each experiment are different at p< 0.05.

Indirect N2O emissions estimated according to (IPCC, 1996a); for every kg of NH3-N volatilised 0.01 kg of N2O-N is formed. \*Indicates cases where indirect N<sub>2</sub>O losses due to volatilised NH<sub>3</sub> are larger than direct (measured) emissions.

Table 5.5. Cumulative (total) ammonia (NH<sub>3</sub>) and nitrous oxide (N<sub>2</sub>O) losses as impacted by slurry dilution in 2003, 2004 and

Experiment	Treatments <sup>2</sup>		Cumul	Cumulative gaseous N losses	N losses	
start date		NH <sub>3</sub> (kg N ha <sup>-1</sup> )	NH <sub>3</sub> loss (% NH <sub>4</sub> <sup>+</sup> -N applied)	$N_2O$ (g N ha <sup>-1</sup> )	$N_2O$ loss (% N applied)	Indirect N <sub>2</sub> O losses (g N ha <sup>-1</sup> )¶
25 Aug 2003	Diluted (25)	9.9 a	2.9	9.3 a	0.004	*66
	Undiluted (0)	12.3 a	8.6	6.8 a	0.003	123*
18 June 2004	Diluted (50)	2.4 b	2.0	190 a	0.113	24
	Undiluted (0)	3.5 a	2.9	185 a	0.110	35
2 Sep 2004	Diluted (100)	4.8 a	4.0	744 a	0.443	48
•	Undiluted (0)	7.2 a	0.9	570 a	0.339	72
21 Sep 2004	Diluted (100)	2.0 b	1.6	105 a	0.063	20
4	Undiluted (0)	4.6 a	3.8	93 a	0.056	46
9 Aug 2005	Diluted (100)	23.2 a	35.1	20.2 a	0.017	232*
)	Undiluted (0)	23.2 a	35.2	25.9 a	0.020	232*
30 Aug 2005	Diluted (100)	7.6 b	11.4	14.5 a	0.012	*92
•	Undiluted (0)	11.3 a	17.1	40.8 a	0.032	113*

Means followed by different letters within the same column and each experiment are different at p< 0.05.

<sup>2</sup> Numbers in brackets are the percentage (%) dilution by volume during each experiment.

Indirect N2O emissions estimated according to (IPCC, 1996a); for every kg of NH3-N volatilised 0.01 kg of N2O-N is formed. \*Indicates cases where indirect N<sub>2</sub>O losses due to volatilised NH<sub>3</sub> are larger than direct (measured) emissions.

Table 5.6. Cumulative (total) ammonia (NH<sub>3</sub>) and nitrous oxide (N<sub>2</sub>O) losses as impacted by rainfall simulation in 2003, 2004 and 2005.

Experiment	Treatments <sup>2</sup>		Cumu	Cumulative gaseous N losses	N losses	
start date	(mm water applied)	NH <sub>3</sub> (kg N ha <sup>-1</sup> )	NH <sub>3</sub> loss (% NH <sub>4</sub> *-N applied)	$N_2O$ (g N ha <sup>-1</sup> )	$N_2O$ loss (% N applied)	Indirect N <sub>2</sub> O losses (g N ha¹¹)¶
2 Sep 2004	Rainfall (6) No rain (0)	2.6 b 7.2 a	2.20	791 a 570 a	0.5	26
21 Sep 2004	Rainfall (6) No rain (6)	2.8 a 4.6 a	2.30	101 a 93.4 a	90.0	28 46
14 Sep 2005	Rainfall (6) No rain (0)	8.9 b 18.2 a	13.5 27.6	20.2 a 25.9 a	0.02	89* 182*
4 Oct 2005	Rainfall (6) No rain (0)	10.5 b 13.9 a	15.8 21.0	26.6 a 45.5 a	0.02	105*

Means followed by different letters within the same column and each experiment are different at p< 0.05.

<sup>2</sup> Numbers in brackets are the amount of water applied during each experiment (mm).

\*Indicates cases where estimated indirect N2O losses due to volatilised NH3 are larger than direct (measured) emissions. Indirect N2O emissions estimated according to (IPCC, 1996a); for every kg of NH3-N volatilised 0.01 kg of N2O-N is formed.

**Table 5.7.** Impact of hog slurry application rate on soil nitrate  $(NO_3^-)$  and ammonium  $(NH_4^+)$ contents (mg N kg<sup>-1</sup> soil) during three separate sampling occasions for selected experiments in 2003, 2004 and 2005¶.

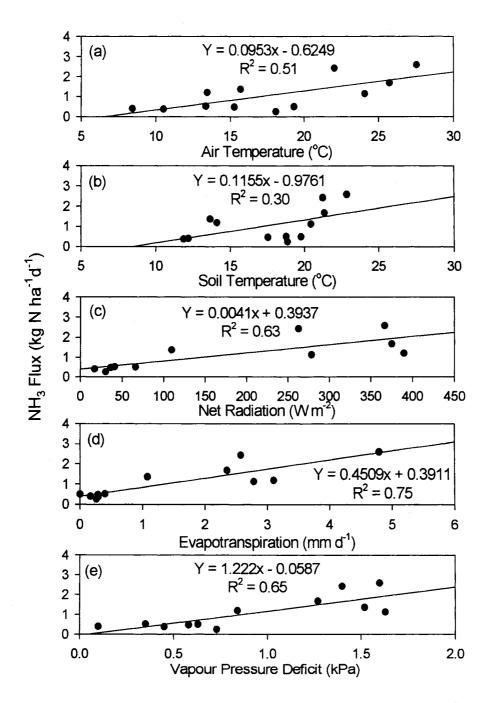
Experiment start date	Slurry rate	=	N (mg kg			-N (mg kg pling occa	
	(L ha <sup>-1</sup> )	1	2	3	1	2	3
6 June 2003	60,000	0.10	1.12	24.2	34.8	56.0	46.4
		(0.05)	(0.55)	(6.79)	(8.83)	(7.86)	(7.89)
	120,000	0.42	6.85	54.8	92.8	54.9	79.4
		(0.25)	(3.75)	(24.6)	(27.4)	(18.4)	(21.0)
3 July 2003	60,000	0.05	0.43	0.05	50.5	56.7	49.2
·		(0.00)	(0.38)	(0.00)	(12.6)	(9.70)	(9.85)
	180,000	0.05	0.68	5.05	106	92.7	92.0
		(0.00)	(0.63)	(3.05)	(0.00)	(10.8)	(9.50)
7 June 2004	60,000	3.57	8.00	2.25	10.0	5.03	1.67
	,	(3.52)	(4.20)	(1.53)	(2.50)	(1.27)	(0.32)
	120,000	0.70	9.50	24.6	11.3	9.63	4.63
	•	(0.65)	(3.30)	(7.98)	(2.37)	(0.74)	(0.98)
18 Oct 2004	60,000	0.05	0.24	1.52	74.1	80.5	43.4
	•	(0.00)	(0.18)	(0.78)	(6.07)	(7.32)	(14.8)
	180,000	0.05	0.70	2.15	93.0	88.9	84.1
		(0.00)	(0.65)	(1.23)	(2.38)	(3.36)	(11.7)
14 Sep 2005	60,000	11.87	_	22.3	31.6	_	2.41
1	,	(9.15)		(14.5)	(31.6)		(2.38)
	180,000	17.00	_	66.2	29.6	_	53.6
	•	(5.94)		(30.9)	(29.5)		(53.6)
4 Oct 2005	60,000	0.53	1.82	1.43	5.05	0.03	4.09
	•	(0.48)	(0.48)	(1.38)	(0.36)	(0.00)	(4.06)
	180,000	0.05	1.90	5.60	40.1	42.3	41.03
		(0.00)	(1.85)	(4.90)	(8.25)	(8.55)	(20.2)

Numbers in brackets are standard errors of the mean (n = 3).

**Table 5.8.** Linear regression results between ammonia ( $NH_3$ ) flux and selected meteorological variables in 2004 and 2005.

Year	Meteorological variable	$\mathbb{R}^2$	P-value	SEM.ª
2004	Air Temperature	0.51	0.01	0.60
	Soil Temperature	0.30	0.07	0.72
	Net Radiation	0.63	0.002	0.51
	Evapotranspiration	0.73	< 0.001	0.42
	Vapour Pressure Deficit	0.65	< 0.002	0.51
2005	Air Temperature	0.63	< 0.001	8.10
	Soil Temperature	0.66	< 0.001	7.72
	Net Radiation	0.69	< 0.001	7.41
	Evapotranspiration	0.48	< 0.001	9.63
	Vapour Pressure Deficit	0.67	<0.001	7.66

<sup>&</sup>lt;sup>a</sup>Standard error of the mean (n = 3).



**Figure 5.1.** Relationship between ammonia (NH<sub>3</sub>) flux (kg N ha<sub>-1</sub> d<sup>-1</sup>) and (a) air temperature (°C), (b) soil temperature (°C), (c) net radiation (W m<sup>-2</sup>), (d) evapotranspiration (mm d<sup>-1</sup>) and vapour pressure deficit (kPa) in 2004.

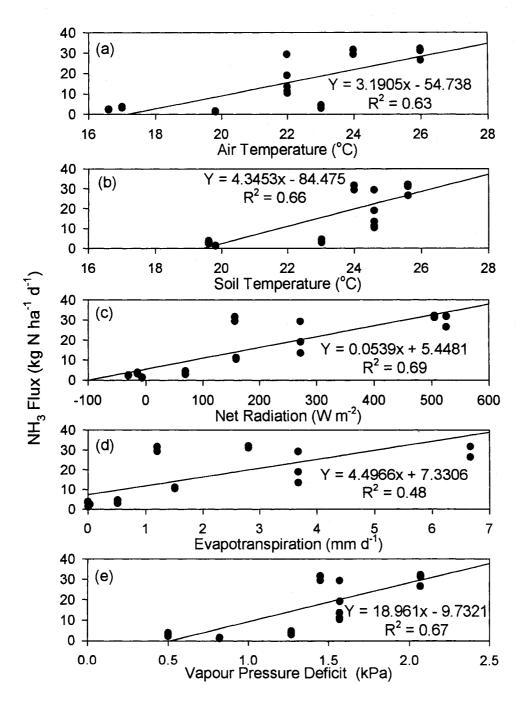


Figure 5.2. Relationship between ammonia (NH<sub>3</sub>) flux (kg N ha<sup>-1</sup> d<sup>-1</sup>) and (a) air temperature (°C), (b) soil temperature (°C), (c) net radiation (W m<sup>-2</sup>), (d) evapotranspiration (mm d<sup>-1</sup>) and (d) vapour pressure deficit (kPa) in 2005.

# **CHAPTER 6**

Nitrous Oxide Emissions and Soil Mineral Nitrogen Status Following Application of
Hog Slurry and Inorganic Fertilisers to Acidic Soils

Materials from this Chapter are drawn from a manuscript which has been submitted for publication in the Canadian Journal of Soil Science.

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## **ABSTRACT**

Field-application of livestock slurry often results in higher nitrous oxide (N<sub>2</sub>O) emissions than inorganic fertiliser, because slurry contains large amounts of available N and C and when applied it increases soil water content, therefore enhancing denitrification. The current study was undertaken to evaluate the impact of hog (Sus scrofa) slurry and inorganic fertilisers on N<sub>2</sub>O emissions and soil inorganic N. Three field experiments were conducted from June to October 2005 on two acidic soils seeded to forage grass. Treatments included Hog Slurry at 60 000 L ha<sup>-1</sup>, Potassium Nitrate at 120 kg N ha<sup>-1</sup>, Ammonium Sulphate at 120 kg N ha<sup>-1</sup>, Carbon (dextrose) at 500 kg ha<sup>-1</sup> and a Control (with neither slurry nor fertiliser). Results from all 3 experiments showed that Potassium Nitrate increased (p<0.05) both N<sub>2</sub>O fluxes and cumulative N<sub>2</sub>O losses compared to the other treatments. Emissions of N<sub>2</sub>O from Slurry and Ammonium were generally similar, but higher (p<0.05) than Carbon and Control, which were statistically similar. Soil NH<sub>4</sub>+N contents were generally similar for the Slurry and Ammonium treatments, but significantly (p<0.05) higher than the other treatments, particularly during the first and second sampling events. Soil NO<sub>3</sub>-N contents meanwhile, were higher (p<0.05) with the Nitrate treatment compared to the other treatments, especially during the first sampling event. Results of this study suggest that NO<sub>3</sub> availability rather than carbon supply was limiting N2O production in these soils. Therefore, N2O emissions from these acid soils can be mitigated by using hog slurry or ammonium-based fertilisers rather than nitrate-based fertilisers.

#### **6.1 INTRODUCTION**

Confined livestock production systems generate substantial quantities of manure, which is managed as either solid or liquid manure. In Canada, most of the manure is eventually applied to agricultural lands and accounts for approximately 10% of agricultural nitrous oxide (N<sub>2</sub>O) emissions (Gregorich et al., 2005). These emissions are a concern because N<sub>2</sub>O is a major greenhouse gas (GHG), and contributes to stratospheric ozone (O<sub>3</sub>) depletion (FAO, 2001).

Nitrous oxide is produced in soils through nitrification and denitrification processes (Granli and Bøckman, 1994). It is generally accepted that compared to inorganic fertilisers, the application of livestock slurry to soil leads to higher N<sub>2</sub>O emissions, particularly when applied to soils low in carbon (C) (Rochette et al., 2000; Velthof et al., 1997). This is due to the fact that slurry contains high amounts of available C and nitrogen (N), and when applied, it creates anaerobic conditions, thus enhancing N<sub>2</sub>O production through denitrification.

Velthof et al. (2003) reported that N<sub>2</sub>O fluxes from different liquid manures were up to 5 times greater than those from ammonium sulphate and ammonium nitrate fertilisers. They reported total N<sub>2</sub>O losses from pig slurries ranging from 7.3 to 13.9% of applied N, while those from inorganic fertilisers ranged from 2.1 to 4.0%. Rochette et al. (2004) found higher N<sub>2</sub>O losses from fall and spring applied pig slurry than ammonium nitrate fertiliser. They reported cumulative N<sub>2</sub>O losses of 1.16, 1.74 and 2.73% of N applied from ammonium nitrate, fall applied hog slurry and spring applied hog slurry, respectively. They suggested that the large amounts of mineral N and easily available organic C in the pig slurry enhanced

denitrification and N<sub>2</sub>O production. Similar findings were also reported by van Groenigen et al. (2004) who observed total N<sub>2</sub>O losses from a sandy soil ranging from 0.04 to 0.13% for calcium ammonium nitrate fertiliser and 0.31 to 0.75% for cattle slurry. Losses from a clay soil ranged from 0.48 to 2.14% for calcium ammonium nitrate and 0.88 to 2.03% for cattle slurry. Ellis et al. (1998), found N<sub>2</sub>O losses higher from cattle slurry than ammonium nitrate fertiliser. In addition, losses were much higher when the slurry was injected rather than surface applied.

In contrast, Velthof et al. (1997) reported lower N<sub>2</sub>O losses from surface applied and injected cattle slurry and ammonium sulphate fertiliser compared to calcium nitrate, calcium ammonium nitrate and urea fertilisers. They postulated that livestock slurry resulted in higher N<sub>2</sub>O losses than mineral fertilisers in soils where organic C was limiting denitrification, while in soils where organic C was not limited, the opposite was true. A similar conclusion was drawn by Rochette et al. (2000) when comparing N<sub>2</sub>O emissions from pig slurry and ammonium nitrate fertiliser. Whalen (2000) found lower N<sub>2</sub>O emissions from liquid swine waste than NH<sub>4</sub><sup>+</sup>-N fertiliser and presumed that some unknown component of liquid swine waste negatively affected the soil microbial community, thus reducing N<sub>2</sub>O emissions.

These contradictory results demonstrate that  $N_2O$  emissions are not only dependent on the type of N applied but also on C availability and other site specific soil properties such as organic matter content, texture and pH. More than 50% of the available N in hog slurry is in the ammonium  $(NH_4^+)$  form, which is rapidly nitrified to nitrate  $(NO_3^-)$  and subsequently denitrified to  $N_2O$  or dinitrogen gas  $(N_2)$ , when conditions are suitable. Previous experiments conducted on the soils used for the current study (Mkhabela et al., 2006), demonstrated that

applying hog slurry resulted in low N<sub>2</sub>O fluxes, even when application rates were as high as 180 t ha<sup>-1</sup> (378 kg N ha<sup>-1</sup>). Understanding the processes that govern N<sub>2</sub>O emissions from slurry applied to acidic soils is essential for the development of N<sub>2</sub>O mitigation strategies.

The objectives of this study were to: (i) assess the impact of hog (Sus scrofa) slurry and mineral fertilisers application on N<sub>2</sub>O emissions and soil mineral N, and (ii) identify the factors that control N<sub>2</sub>O production in acidic soils.

### 6.2 MATERIAL AND METHODS

## 6.2.1 Experimental Location and Site Description

Three separate field experiments were conducted in June, July and September 2005 on two contrasting acidic soils seeded to forage grass in Great Village, Nova Scotia (45°25′N, 63°36′W). One of the soils is classified as an Acadia (Marshland) fine loam (Gleyed Regosol or Regosol, Canadian and FAO classification), while the other is a Hebert sandy-skeletal (Orthic Humo-Ferric Podzol or Orthic Podzol, Canadian and FAO classification) (AAFC, 1998a). Acadia soils are developed on strongly to slightly acid deep level silt loam to silty clay loam, marine sediments and have slow to extremely slow permeability (Webb, et al., 1991). Acadia soils were reclaimed from salt marsh and dyked to protect them from tidal flooding and are mainly used for forage grass production. Meanwhile, Hebert soils have developed on coarse loamy-gravel over sandy to sandy skeletal, strongly acidic glacio-fluvial sediments and are rapidly to well drained (Webb, et al., 1991). Physical and chemical characteristics of both soils are shown in Table 6.1. The forage grass was a mixture of timothy (*Phleum pratense*) and meadow fescue (*Festuca pratensis*).

## 6.2.2 Experimental Design and Treatments

In all three experiments, treatments were arranged in a randomised complete block (RCB) design (Appendix 5). In experiment 1 the treatments consisted of (i) hog slurry (Slurry) applied at 126 kg total N ha<sup>-1</sup>, (ii) ammonium sulphate (Ammonium) applied at 120 kg N ha<sup>-1</sup> and (iv) a control (Control) where neither slurry or fertiliser were applied. In experiments 2 and 3, the same treatments and rates were used. The only difference however, was that another treatment was included, where carbon (Carbon) without fertiliser or slurry was added as Dextrose at a rate of 500 kg ha<sup>-1</sup>, giving a total of five treatments. Treatments in experiment 1 were replicated four times, while in experiments 2 and 3 they were replicated three times. Plot sizes for all experiments were 1 m × 1 m separated by 1-m. Experiments 1 and 3 were conducted on the Hebert soil while experiment 2 was conducted on the Acadia soil. Both fertiliser and slurry were manually applied. Slurry was applied using watering cans to obtain an even distribution. The slurry was collected from a nearby commercial hog-sow operation and its characteristics are provided in Table 6.1. Measurement of N<sub>2</sub>O emissions started soon (approximately 30 min) after application of treatments.

## 6.2.3 Nitrous Oxide Emissions Measurements

Nitrous oxide emissions were measured using vented static chambers made from polyvinyl chloride (PVC) (Appendix 2b). The chambers consisted of a collar (bottom) and a top (chamber). The collars measured 20 cm inside diameter × 10 cm height while the chambers measured 20 cm inside diameter × 15 cm height. The chambers were insulated with

foam plastic lined with aluminium foil to minimise temperature increase inside the chamber during sampling. Soon after application of treatments, one collar per plot was inserted to the soil to a depth of approximately 5 cm and left open to the atmosphere throughout the duration of each experiment. During sampling, chambers were attached to the collars and 20-mL gas samples were collected through a rubber septum at regular intervals (0, 10, 20 and 30 min) using plastic disposable syringes (Becton-Dickinson, Franklin Lakes, NJ) and subsequently transferred to 12 mL pre-evacuated vials (Labco Exetainer, High Wycombe, UK) which were sealed with silicone to prevent gas leakage and kept until analysis. Prior to gas sampling, head-space gas was thoroughly mixed by pumping several times with the syringe. Gas samples were collected once a day for 2-3 d starting immediately after application of treatments, and thereafter at an increasing interval for a maximum of 21 d. Nitrous oxide concentrations were analysed using a Varian GP3800 gas chromatograph (GC) fitted with an electron capture detector (Varian Inc., Palo Alto, CA). The N<sub>2</sub>O emission (flux) per chamber was calculated assuming a linear increase in gas concentration (Hutchinson and Livingston, 1993):

$$F_{N2O} = \frac{dC}{dT} x \frac{V}{A} x \frac{M}{V_{mol}}$$
 (1)

where  $F_{N2O}$  is the rate of  $N_2O$  flux ( $\mu g$  of  $N_2O$  m<sup>-2</sup> min<sup>-1</sup>), dC/dT is the rate of change of  $N_2O$  concentration within the chamber ( $\mu$ mol mol<sup>-1</sup> min<sup>-1</sup>), V is the chamber head-space volume (m³), A is the surface area of the chamber (0.031 m²), M is the molecular weight of  $N_2O$  (44 g mol<sup>-1</sup>) and  $V_{mol}$  is the volume of a mole of gas at 20°C (0.024 m<sup>-3</sup> mol<sup>-1</sup>).

### 6.2.4 Soil Sampling and Analysis

Soil samples for NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N analysis were collected 3 times during each experiment. In experiment 1, soil samples were collected 4, 11 and 20 d after application, while in experiment 2 they were collected 3, 12 and 21 d after application. In experiment 3, samples were collected 2, 10 and 20 d after application. During soil sampling, three samples plot<sup>-1</sup> (0-15 cm depth) were collected and mixed to make a composite sample using a handheld auger and placed in pre-labeled soil plastic bags. Samples were air-dried and passed through a 2-mm mesh screen. Sub-samples of 5 g were shaken with 50 mL of 2M KCl for 45 min and the soil suspensions filtered through Whatman No. 42 filter papers. Filtrates were kept frozen until analysis for NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N using a Technicon auto-analyser (Technicon Instruments, Tarrytown, NY) following the method of Keeney and Nelson (1982). The detection limits for NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N were 0.03 and 0.05 mg L<sup>-1</sup>, respectively.

Volumetric soil water content ( $\theta_v$ ) at 0-20 cm depth and soil temperature at 0-10 cm depth were determined on each gas sampling date using a hand held time domain reflectometer (TDR) (Campbell Scientific Corp., Logan, UT) and an Oakton thermometer (Oakton Instruments, Vernon Hills, IL), respectively. Soil bulk density (BD) at each site was determined at the beginning of each experiment using the core method. Four soil cores were extracted using aluminium tubes measuring 5 cm inner diameter  $\times$  15 cm length. The soil cores were oven-dried for 48 h at 105 °C. Total porosity ( $P_i$ ) was calculated assuming a particle density of 2.65 Mg m<sup>-3</sup>. Percent water filled pore space (%WFPS) was calculated as follows:

$$\%WFPS = (\theta_v / P_t) \times 100^{\circ}$$
 (2)

### 6.2.5 Statistical Analysis

All data were subjected to analysis of variance (ANOVA) using the PROC GLM function of the SAS statistical programme (SAS Institute, 1996). For both N<sub>2</sub>O flux and soil mineral N, data from each sampling day were analysed separately and differences among treatments were declared to be significant at p<0.05. Cumulative N<sub>2</sub>O losses were calculated by integrating N<sub>2</sub>O losses measured between sampling periods. Due to high variability and violation of the normality and constant variance assumptions, N<sub>2</sub>O data were log-transformed before analysis. When there was a significant treatment effect, means were compared using Duncan Multiple Range test (DMRT).

#### 6.3 RESULTS AND DISCUSSION

#### 6.3.1 Soil Mineral N Status

In experiment 1, during the first and second soil sampling events the Slurry and Ammonium treatments had higher (p<0.05) soil NH<sub>4</sub><sup>+</sup>-N contents compared to the Nitrate and Control treatments. The Slurry and Ammonium treatments, however, were similar (Table 6.2). The NH<sub>4</sub><sup>+</sup>-N concentrations in the Slurry and Ammonium treatments decreased with time such that by the last sampling day (20 d after application) all treatments had similar (p> 0.05) soil NH<sub>4</sub><sup>+</sup>-N concentrations. Meanwhile, application of Nitrate resulted in higher (p<0.05) soil NO<sub>3</sub><sup>-</sup>-N concentration compared to the other treatments during the first sampling (4 d after application). However, during the second sampling period (10 d after application) all treatments had similar (p> 0.05) soil NO<sub>3</sub><sup>-</sup>-N concentrations except for the Control (Table 6.2). Nitrate-N concentration from Nitrate decreased with time, while with

Slurry and Ammonium concentrations slightly increased with time. By the last sampling period (20 d after application), Slurry had higher (p<0.05) NO<sub>3</sub>-N concentrations (11 mg kg<sup>-1</sup>) than other treatments, which had similar levels of soil NO<sub>3</sub>-N (~5 mg kg<sup>-1</sup>).

The soil  $NH_4^+$ -N concentrations in experiment 2 followed a trend similar to experiment 1. The values were much higher however, during the first sampling period. In all three sampling periods, Ammonium and Slurry resulted in higher (p<0.05) soil  $NH_4^+$ -N concentrations relative to the other treatments (Table 6.2). Generally, Ammonium had higher  $NH_4^+$ -N concentrations during all sampling times compared to Slurry, but was only significant (p<0.05) during the last (third) sampling period. The  $NH_4^+$ -N concentrations from all treatments decreased with time, with Ammonium being the only exception when it increased during the last sampling period. Soil  $NO_3^-$ -N concentrations meanwhile, were only significantly (p<0.05) affected by treatments during the first sampling period (2 d after application), with Nitrate having higher  $NO_3^-$ -N compared to the other treatments (Table 6.2). Soil  $NO_3^-$ -N in the Slurry treatments slightly increased with time to a high of 8 mg kg<sup>-1</sup>, while for the remaining treatments it decreased to a low of ~ 1 mg kg<sup>-1</sup>.

In experiment 3, Ammonium and Slurry had higher (p<0.05) soil NH<sub>4</sub><sup>+</sup>-N contents compared to the other treatments in all sampling dates, the only exception was in the third sampling period (20 d after application) when the NH<sub>4</sub><sup>+</sup>-N content from Slurry and Nitrate were similar (Table 6.2). The soil NH<sub>4</sub><sup>+</sup>-N concentrations from both Ammonium and Slurry decreased with time, while those for the other treatments remained constant. Soil NO<sub>3</sub><sup>-</sup>-N concentrations meanwhile, were affected (p<0.05) by treatments in all sampling occasions (Table 6.2). During the first and second sampling periods (2 and 12 d after application)

Nitrate treatment had higher (p<0.05) soil NO<sub>3</sub><sup>-</sup>-N (Table 6.2). During the third sampling period (20 d after application) however, Ammonium and Slurry had higher (p<0.05) soil NO<sub>3</sub><sup>-</sup>-N concentrations than Control, Carbon and Nitrate, which had similar (p>0.05) concentrations. Generally, NO<sub>3</sub><sup>-</sup>-N concentrations from Control, Nitrate and Carbon decreased with time, while Ammonium and Slurry slightly increased with time. Surprisingly, both the Control and Carbon treatments, which received no fertiliser or slurry had higher soil NO<sub>3</sub><sup>-</sup>-N concentrations; although not significant compared to Slurry and Ammonium during the first sampling (2 d after application) period (Table 6.2). In addition, Nitrate had a high (187 mg kg<sup>-1</sup>) NO<sub>3</sub><sup>-</sup>-N content during the first sampling date. These high values might have been due to contamination of the soil samples, since these values did not necessarily result in higher N<sub>2</sub>O fluxes from these treatments on this day.

The higher (p<0.05) soil NH<sub>4</sub><sup>+</sup>-N concentrations from plots that received Slurry compared to Nitrate, Carbon and Control in all three experiments, coupled with the generally similar soil NH<sub>4</sub><sup>+</sup>-N contents for Slurry and Ammonium, shows that hog slurry was a valuable source of NH<sub>4</sub><sup>+</sup>-N. The addition of Slurry however, did not increase NO<sub>3</sub><sup>-</sup>-N contents in the soil compared to Ammonium, Carbon and Control, indicating that hog slurry was a poor source of NO<sub>3</sub><sup>-</sup>-N. In Quebec, Rochette et al. (2004) observed that the addition of pig slurry at 200 kg N ha<sup>-1</sup> only increased NH<sub>4</sub><sup>+</sup>-N but not NO<sub>3</sub><sup>-</sup>-N, while the addition of ammonium nitrate fertiliser increased both soil NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N. Similarly, Sherlock et al. (2002) observed an increase in NH<sub>4</sub><sup>+</sup>-N in the soil but a slight or no increase in NO<sub>3</sub><sup>-</sup>-N after applying pig slurry at a rate of 60 m<sup>-3</sup> ha<sup>-1</sup> to a pasture soil (pH 5.4) in New Zealand. Chantigny et al. (2004a) suggested that large increases in soil NO<sub>3</sub><sup>-</sup>-N content following slurry application are

often a result of rapid nitrification of slurry NH<sub>4</sub><sup>+</sup>-N. In a laboratory study, Dendooven et al. (1998) observed low NO<sub>3</sub><sup>-</sup>-N after applying hog slurry and postulated that some compounds in the slurry (e.g. antibiotics) inhibited nitrification.

In the current study, a decrease in the soil NH<sub>4</sub><sup>+</sup>-N content over time in all three experiments was not accompanied by a simultaneous increase in soil NO<sub>3</sub>-N concentrations. This suggests that nitrification was not a major consumer of NH<sub>4</sub><sup>+</sup>-N, probably due to the low soil pH. Low soil pH is known to inhibit nitrification, with maximum nitrification rates occurring at a pH range of 7-8 (Dalal et al., 2003; Granli and Bøckman, 1994). In addition, the loss of NH<sub>4</sub><sup>+</sup>-N through fixation by clay, plant uptake and NH<sub>3</sub> volatilisation may have also contributed to the low soil NO<sub>3</sub>-N. Fixation of slurry NH<sub>4</sub>+N by clay can be substantial and it can rapidly happen soon after pig slurry application. Chantigny et al. (2004b) observed that 6 h after pig slurry application, 11 and 34% of applied slurry NH<sub>4</sub><sup>+</sup>-N was fixed by a sandy and clay soil, respectively. Meanwhile, Morvan et al. (1997) reported that the uptake of NH<sub>4</sub><sup>+</sup>-N from pig slurry by ryegrass and its loss through NH<sub>3</sub> volatilisation can be as high as 33 and 40% of applied NH<sub>4</sub>-N, respectively. However, such high losses through NH<sub>3</sub> volatilisation in the current study are unlikely due to the low soil and slurry pH (Table 6.1). Acidifying slurry to a pH of 5.0 to 6.5 before field-application has been shown to reduce NH<sub>3</sub> volatilisation by 50 to 75% (Rotz, 2004; Vandre and Clemens, 1997). Therefore, it is more likely that some of the NH<sub>4</sub><sup>+</sup>-N was fixed by the soil and also taken up by the grass (Morvan et al., 1997). Nevertheless, the lower N<sub>2</sub>O fluxes (discussed below) from Ammonium and Slurry relative to Nitrate in all three experiments may be partly explained by the low soil NO<sub>3</sub> -N contents in the days following applications.

### 6.3.2 Daily N<sub>2</sub>O Fluxes

Daily N<sub>2</sub>O fluxes, rainfall and WFPS in experiment 1 are shown in Figure 6.1. The N<sub>2</sub>O fluxes for the Control were lowest relative to other treatments. During two sampling dates (6 and 18 June) fluxes from this treatment were negative. Fluxes from the Slurry and Ammonium treatments were generally similar in magnitude. During the early part of the experiment however, fluxes from the Ammonium treatment were higher (p<0.05) than from the Slurry. Fluxes from the Nitrate treatment were higher (p<0.05) than all other treatments, particularly during the initial days of the experiment, indicating that NO<sub>3</sub> availability was the driving force for N<sub>2</sub>O production in this soil. Fluxes from the Nitrate treatment increased following a 27 mm rainfall event on 6 June (Figure 6.1), suggesting that the majority of the N<sub>2</sub>O was produced through denitrification. The highest fluxes (48 g N ha<sup>-1</sup> d<sup>-1</sup>) were recorded on 3 and 9 June from the Nitrate treatment, and thereafter the fluxes decreased to similar magnitudes as the Slurry and Ammonium treatments. The highest fluxes for Slurry and Ammonium treatments were 6 and 9 g N ha<sup>-1</sup> d<sup>-1</sup>, respectively. Ellis et al. (1998) recorded maximum N<sub>2</sub>O fluxes of 13 and 9 g N ha<sup>-1</sup> d<sup>-1</sup> after applying ammonium nitrate and cattle slurry, respectively, to a pasture soil in the United Kingdom.

In experiment 2,  $N_2O$  fluxes followed a pattern similar to experiment 1 but with greater magnitudes (Figure 6.2). The Control and Carbon treatments had lower (p<0.05) fluxes than the other treatments for most days. Most of the time, fluxes from Control and Carbon were negative and never went above 6 g N ha<sup>-1</sup> d<sup>-1</sup>. The Nitrate and Ammonium treatments did not have negative fluxes. Similar to experiment 1, Nitrate had higher (p<0.05) fluxes relative to the other treatments, particularly during the initial part of the experiment.

The highest flux (955 g N ha<sup>-1</sup> d<sup>-1</sup>) from this treatment was recorded 3 d after application following 14 and 5 mm rainfall events on 14 and 15 July, respectively (Figure 6.2). This suggests that N<sub>2</sub>O production in this acid soil is driven by NO<sub>3</sub> availability and rainfall and that the majority of the N<sub>2</sub>O emitted was produced mainly through denitrification. These high fluxes from the Nitrate treatment are comparable to Dobbie and Smith (2003) who recorded N<sub>2</sub>O fluxes as high as 1200 g N ha<sup>-1</sup> d<sup>-1</sup> following application of inorganic N fertiliser to British grassland soils. The Slurry had the lowest flux (-0.16 g N ha<sup>-1</sup> d<sup>-1</sup>) 4 d after application and thereafter fluxes increased reaching a maximum (189 g N ha<sup>-1</sup> d<sup>-1</sup>) at 17 d. This was probably the result of slow nitrification of slurry NH<sub>4</sub><sup>+</sup>-N. Generally, fluxes from Slurry were slightly higher than those from Ammonium, which had a highest flux (72 g N ha<sup>-1</sup> d<sup>-1</sup>) on the last day of the experiment (21 d after application), further indicating reduced nitrification activity. Sherlock et al. (2002) also observed low N<sub>2</sub>O fluxes (24 g N ha<sup>-1</sup> d<sup>-1</sup>) in the first 14 d following pig slurry application and attributed this to low soil NO<sub>3</sub>-N. They further reported that after the first 14 d, fluxes increased to a peak of 180 g N ha<sup>-1</sup> d<sup>-1</sup> and this increase coincided with an increase in soil NO<sub>3</sub>-N content.

Daily N<sub>2</sub>O fluxes in experiment 3 were lower than in experiment 2 but relatively similar to experiment 1 (Figure 6.3). As in experiments 1 and 2, the Nitrate treatment had higher (p<0.05) fluxes, confirming that N<sub>2</sub>O production in these soils was controlled by NO<sub>3</sub><sup>-1</sup> availability. Fluxes from Nitrate ranged from 0.3 to 35 g N ha<sup>-1</sup> d<sup>-1</sup>, with the highest flux recorded 4 d after application following a 22 mm rainfall event on 26 September (Figure 6.3). Fluxes from Slurry and Ammonium followed a similar pattern and ranged from -0.4 to 8.9 g N ha<sup>-1</sup> d<sup>-1</sup> for Slurry and 0.1 to 3.9 g N ha<sup>-1</sup> d<sup>-1</sup> for Ammonium. Interestingly, fluxes from both

these treatments peaked 14 d after application, probably due to low nitrification activity. Throughout the measurement period, Control and Carbon recorded the lowest fluxes, with fluxes ranging from -1.3 to 0.5 g N ha<sup>-1</sup> d<sup>-1</sup>, further confirming that  $N_2O$  production in these soils is limited by  $NO_3^-$  availability.

The lower (p<0.05) N<sub>2</sub>O fluxes from Slurry relative to Nitrate treatments in all three experiments were not expected. It is generally acknowledged that livestock slurry enhances N<sub>2</sub>O emissions compared to inorganic fertiliser since it contains substantial available N and C and when applied it creates anaerobic conditions, thus enhancing denitrification (Granli and Bøckman, 1994; Rochette, et al., 2004). The lower N<sub>2</sub>O fluxes from Slurry observed were possibly the result of restricted NO<sub>3</sub> supply due to low nitrification in these acidic soils. Most of the inorganic N in the slurry was in the NH<sub>4</sub>+ form (52% of total N), which had to be converted to NO<sub>3</sub> by nitrifying organisms before being denitrified to N<sub>2</sub>O and/ or N<sub>2</sub>. Soil pH is a secondary controller of denitrification by mainly affecting the nitrification process, with optimum nitrification rates occurring at soil pH of 7 to 8 (Dalal et al., 2003; Granli and Bøckman, 1994). This is supported by the fact that the Ammonium treatment also had lower (p<0.05) N<sub>2</sub>O fluxes than the Nitrate treatment. Additionally, soil NO<sub>3</sub>-N concentrations in the Ammonium and Slurry treatments remained lower (p<0.05) than in the Nitrate treatment, especially during the initial sampling period.

Even though this study was not designed to compare N<sub>2</sub>O fluxes between experiments, it is noteworthy that fluxes were higher in experiment 2 than in experiments 1 and 3. This was probably due to differences in chemical characteristics of the two soils and the higher WFPS in experiment 2. van Groenigen et al. (2004) observed higher N<sub>2</sub>O losses

from a clay soil compared to a sandy soil after applying cattle slurry and mineral fertiliser. They attributed this to higher WFPS in the clay soil. In the current study, WFPS in experiment 2 remained generally > 80% throughout the gas measurement period, while in experiments 1 and 3 it was generally < 60% (Figures 6.1, 6.2 and 6.3). Previous studies have shown that large  $N_2O$  fluxes occurred when WFPS was >60% (Dobbie and Smith, 2003; Maag and Vinther, 1999; Velthof and Oenema, 1995). High WFPS (80-90%) limits oxygen  $(O_2)$  diffusion into the soil, creating anaerobic conditions and hence increasing  $N_2O$  production through denitrification.

The low  $N_2O$  fluxes from Control and Carbon coupled with the higher fluxes from Nitrate in all experiments indicate that  $N_2O$  production in these acid soils is limited by  $NO_3$  availability, not carbon. The higher  $N_2O$  fluxes from Nitrate compared to Ammonium and Slurry suggest that the majority of the  $N_2O$  from these soils was produced through denitrification.

### 6.3.3 Cumulative N<sub>2</sub>O Losses

Cumulative N<sub>2</sub>O losses from the Nitrate treatment were higher (p<0.05) than other treatments in each experiment, the only exception was experiment 2 when losses from Nitrate and Slurry were not different (Table 6.3). Losses from Control and Carbon were lower (p<0.05) than all other treatments for all experiments, with losses ranging from approximately -1 to 39 g N<sub>2</sub>O-N ha<sup>-1</sup>. Losses from Ammonium and Slurry were generally statically similar. Results of the current study agree with Velthof et al. (1997) who found higher total N<sub>2</sub>O losses from calcium ammonium nitrate (CAN) and calcium nitrate (CN) fertilisers compared

to cattle slurry applied to a poorly drained sandy soil used for grass production in the Netherlands.

After subtracting the control, cumulative N<sub>2</sub>O losses from Nitrate were 460, 3647 and 202 g N<sub>2</sub>O-N ha<sup>-1</sup> for experiments 1, 2 and 3, respectively (Table 6.3). These losses accounted for 0.38, 3.04 and 0.17% of applied fertiliser N, respectively. Losses from Ammonium in experiment 1, 2 and 3 were 135, 442 and 45 g N<sub>2</sub>O-N ha<sup>-1</sup>, respectively, accounting for 0.11, 0.37 and 0.04% of applied fertiliser N, respectively. In the Netherlands, Velhoft and Oenema (1995) observed total N<sub>2</sub>O losses ranging from 0.5 to 3.9% of N applied as CAN to several grassland soils, while Velhoft et al. (1997) observed N<sub>2</sub>O losses amounting to 8.3 and 12.0% on N applied as CAN and CN, respectively. Losses from the Slurry treatment were 88, 1900 and 89 g N<sub>2</sub>O-N ha<sup>-1</sup> for experiments 1, 2 and 3, respectively, representing 0.07, 1.51 and 0.07% of applied slurry N, respectively (Table 6.3). These losses are comparable to Chadwick et al. (2000) who over 20 d of measurements observed total N<sub>2</sub>O losses ranging from 0.05 to 0.97% of N applied as cattle and pig slurry to grassland in England, and also to Velhoft et al. (1997) who recorded losses <0.1% after applying cattle slurry to a grassland soil in the Netherlands. Whalen (2000), in experiments that lasted 8 or 11 d, recorded total N<sub>2</sub>O losses ranging from 0.05 to 1.0% of total N applied as inorganic N fertiliser or liquid swine waste. Results from the current study therefore suggest that, N<sub>2</sub>O losses from these soils are controlled by NO<sub>3</sub> availability and therefore can be minimised by using hog slurry or ammonium-N based fertilisers rather than nitrate-N based fertilisers.

## **6.4 CONCLUSIONS**

This study has demonstrated that the addition of hog slurry and ammonium sulphate fertilisers to two acidic soils results in significantly lower N<sub>2</sub>O fluxes and subsequently lower total N<sub>2</sub>O losses compared to potassium nitrate fertiliser. Most importantly, the study has shown that NO<sub>3</sub>-N availability is the main driver for N<sub>2</sub>O production in these acidic soils. Therefore, N<sub>2</sub>O emissions from these soils can be mitigated by using hog slurry or NH<sub>4</sub> based fertilisers, rather than NO<sub>3</sub> based fertilisers. Long-term field studies (covering one whole growing season or more) are required to verify these findings, since mineralisation and nitrification of slurry-N over time may have an influence on N<sub>2</sub>O production over a longer period compared to inorganic fertiliser.

Table 6.1. Chemical and physical characteristics of the soils (0-20 cm depth) and hog slurry

used in the study.

<del></del>	<del></del>		
Characteristic	Hebert Soil	Acadia Soil	Hog Slurry
pН	6.50#	5.13#	5.55
TN (%)	0.16	0.27	0.21
C (%)	3.91	3.15	1.44
C:N ratio	24.4	11.7	6.9
$NH_4^+-N$ (%)	nd	nd	0.11
$NO_3^-$ -N (mg kg <sup>-1</sup> )	4.40	1.57	nd
Dry Matter (%)	na	na	4.73
Porosity (%)	52.5	53.2	na
Bulk Density (Mg m <sup>-3</sup> )	1.26	1.24	na
Organic Matter (%)	4.10	4.30	na
CEC (meq/100g)	10.6	18.7	na

nd = not determined, na = not applicable, \*pH 1:2 dry soil: de-ionised water, TN and C determined using CNS analyser.

**Table 6.2.** Soil NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N concentrations from Control, Carbon, Potassium Nitrate (Nitrate), Ammonium Sulphate (Ammonium) and Hog Slurry (Slurry) treatments at different sampling periods for experiments 1, 2 and 3.

Treatments	Soil NH <sub>4</sub> +-N (mg kg <sup>-1</sup> )		Soil NO <sub>3</sub> -N (mg kg <sup>-1</sup> )			
	Sampling I	Sampling 2	Sampling 3	Sampling I	Sampling 2	Sampling 3
Experiment 1		•		<u>.</u>		
Control	8.94 b	6.68 b	2.48 a	6.70 b	7.66 b	4.53 b
Nitrate	8.58 b	6.82 b	4.30 a	47.00 a	16.15 a	5.80 b
Ammonium	29.88 a	11.43 a	7.15 a	9.35 b	13.16 a	5.67 b
Slurry	23.87 a	14.02 a	4.75 a	5.61 b	13.96 a	11.81 a
Experiment 2						
Control	15.73 b	8.47 b	5.57 c	6.96 b	1.87 a	0.05 a
Carbon	15.23 b	9.25 b	6.53 bc	5.16 b	1.47 a	0.05 a
Nitrate	12.54 b	7.80 b	5.48 c	40.25 a	11.86 a	0.11 a
Ammonium	65.86 a	32.62 a	43.99 a	3.44 b	5.28 a	3.35 a
Slurry	37.78 a	25.61 a	14.09 b	3.10 b	5.84 a	7.86 a
Experiment 3						
Control	3.50 b	3.32 b	3.05 c	36.90 b	2.39 c	4.48 b
Carbon	0.22 c	0.37 c	0.72 d	26.73 b	4.22 bc	5.83 b
Nitrate	5.58 b	7.77 b	8.08 bc	186.84 a	17.74 a	4.97 b
Ammonium	85.83 a	65.52 a	45.71 a	8.13 b	5.93 b	9. <b>84</b> a
Slurry	67.60 a	32.36 a	15.21 ab	4.16 b	4.29 bc	9.85 a

Means followed by the same letter within each column and each experiment are not significantly different (p> 0.05) using DMRT.

**Table 6.3.** Cumulative N<sub>2</sub>O losses from Control, Carbon, Potassium Nitrate (Nitrate), Ammonium Sulphate (Ammonium) and Hog Slurry (Slurry) treatments in experiments 1, 2 and 3.

Treatments	Gross N <sub>2</sub> O loss (g N ha <sup>-1</sup> )	Net N <sub>2</sub> O loss (g N ha <sup>-1</sup> )	N lost as N <sub>2</sub> O (%)	
Experiment 1				
Control	4.41 c			
Nitrate	464.72 a	460.31	0.38	
Ammonium	139.14 b	134.73	0.11	
Slurry	88.37 b	83.96	0.07	
Experiment 2				
Control	39.34 c			
Carbon	2.71 c	_		
Nitrate	3686.06 a	3646.72	3.04	
Ammonium	481.37 b	442.03	0.37	
Slurry	1939.96 ab	1900.62	1.51	
Experiment 3				
Control	-1.48 c	•		
Carbon	-1.12 c	<u>—</u>	<del></del>	
Nitrate	200.70 a	202.18	0.17	
Ammonium	43.53 b	45.01	0.04	
Slurry	87.77 b	89.25	0.07	

Means followed by the same letter within each column and each experiment are not significantly different (p> 0.05) using DMRT.

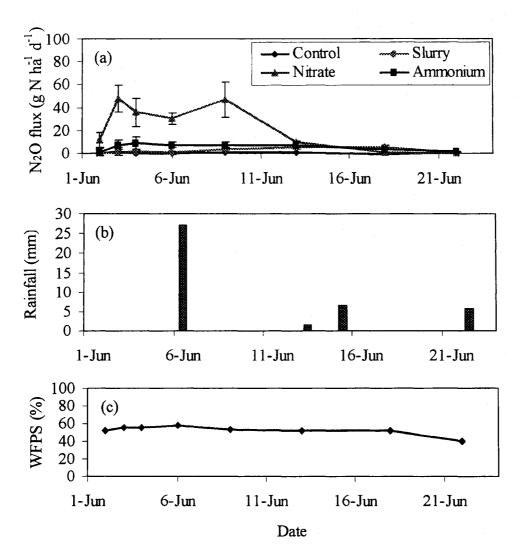
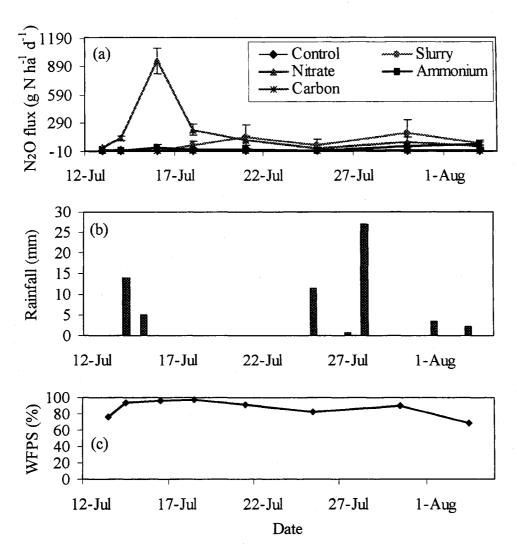


Figure 6.1. Daily  $N_2O$  fluxes (a), daily rainfall (b) and daily soil water-filled pore space (c) over a 21-d measurement period in experiment 1. Vertical bars represent standard error (n = 4) (note, some bars are smaller than symbols).



**Figure 6.2.** Daily  $N_2O$  fluxes (a), daily rainfall (b) and daily soil water-filled pore space (c) over a 21-d measurement period in experiment 2. Vertical bars represent standard error (n = 3) (note, some bars are smaller than symbols).

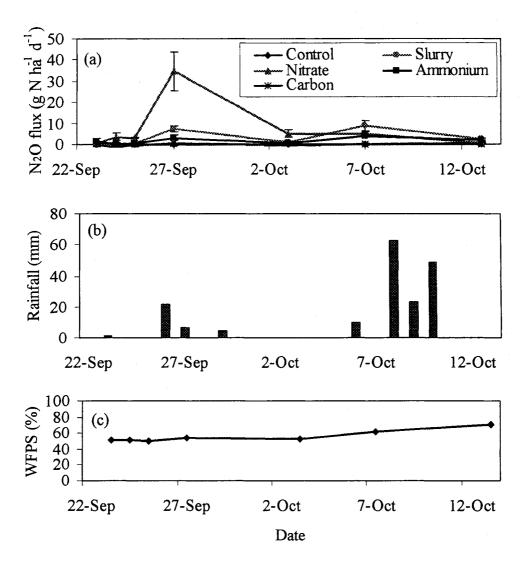


Figure 6.3. Daily  $N_2O$  fluxes (a), daily rainfall (b) and daily soil water-filled pore space (c) over a 20-d measurement period in experiment 3. Vertical bars represent standard error (n = 3) (note, some bars are smaller than symbols).

# **CHAPTER 7**

Gaseous and Leaching Nitrogen Losses from No-Tillage and Conventional Tillage

Systems Following Surface Application of Cattle Manure

Materials from this Chapter are drawn from a manuscript that has been submitted for publication in Soil and Tillage Research.

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#### **ABSTRACT**

Previous studies have demonstrated inconsistent results on the impact of tillage systems on nitrogen (N) losses from field-applied manure. This study assessed the impact of no-tillage (NT) and conventional tillage (CT) systems on gaseous N losses, N2O:N2O+N2 ratios and NO<sub>3</sub>-N leaching following surface application of cattle manure. The study was undertaken during the 2003/04 and 2004/05 seasons at two field sites in Nova Scotia namely, Streets Ridge (SR) in Cumberland County and the Bio-environmental Engineering Centre (BEEC) in Truro. Results showed that the NT system had higher (p< 0.05) NH<sub>2</sub> losses than CT. Over the two seasons, manure incorporation in CT reduced NH<sub>3</sub> losses on average by 86% at SR and 78% at BEEC relative to NT. At both sites and during both seasons, denitrification rates and N<sub>2</sub>O emissions in NT were generally higher than in CT plots, probably due to higher soil water and organic matter content in NT. Conversely, N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratios were lower in NT than CT suggesting more complete reduction of N<sub>2</sub>O to N<sub>2</sub> under NT. When averaged across all soil depths,  $NO_3$ -N was higher (p<0.05) in CT than NT. Nitrate-N decreased with depth at both sites regardless of tillage. In most cases, NO<sub>3</sub>-N was higher under CT than NT at all soil depths. Similarly, flow weighted average NO<sub>3</sub>-N concentrations in drainage water were generally higher under CT. This may partly be attributed to higher denitrification rates under NT. Therefore, NT may be a viable strategy to remove NO<sub>3</sub>-N from the soil, and thus, reduce NO<sub>3</sub>-N contamination of groundwater. However, it should be noted that the use of NT to reduce NO<sub>3</sub>-N leaching may actually increase NH<sub>3</sub> and N<sub>2</sub>O emissions resulting in negative net benefits.

#### 7.1 INTRODUCTION

No-tillage (NT) systems are being promoted as superior to conventional tillage (CT) as they improve soil structure, increase soil moisture, reduce erosion and subsequently increase yields and economic benefits to the producer. However, some reports have shown that NT systems may increase NH<sub>3</sub> and N<sub>2</sub>O emissions as well as NO<sub>3</sub>-N leaching, while others have reported the opposite or no difference. For example, Aulakh et al. (1984), MacKenzie et al. (1997; 1998) and Skiba et al. (2002) found higher N<sub>2</sub>O fluxes with NT than CT. Linn and Doran (1984) reported that N<sub>2</sub>O production from NT was 9.4 times greater than from CT. On the contrary, Passianoto et al. (2003) reported lower N<sub>2</sub>O emissions with NT as losses over 6 months were estimated to be 1.6 and 2.23 kg N ha-1 for NT and CT, respectively. Similarly, Drury et al. (2006) found lower N<sub>2</sub>O losses with NT in a three year field study in Ontario. Meanwhile, Elmi et al. (2003) and Grandy et al. (2006a) reported no difference in N<sub>2</sub>O emissions between CT and NT in Quebec and Michigan, respectively. Helgason et al. (2005), when reviewing Canadian data found that N<sub>2</sub>O emissions were in most cases higher under NT than CT in eastern Canada (humid climate), while in western Canada (arid and semi-arid climate) the opposite was often observed.

Boddy and Baker (1990) and Schreiber and Cullum (1992) reported higher NO<sub>3</sub>-N losses under NT, while Elmi et al. (2003) found that tillage system had no effect on NO<sub>3</sub>-N losses. Paul and Clark (1989), suggested that good soil conservation practices, such as NT, reduce NO<sub>3</sub>-N losses in surface runoff, but result in increased NO<sub>3</sub>-N drainage losses through leaching. The NT system encourages the formation of continuous soil macro-pores, which may increase NO<sub>3</sub>-N preferential flow. Conversely, some studies have reported NO<sub>3</sub>-N

leaching to be higher under CT due to either increased N mineralisation under CT or greater denitrification under NT (Angle et al., 1993; Varshney et al., 1993; Randall and Iragavarapu, 1995; Patni et al., 1998).

Denitrification is a major process for soil N<sub>2</sub>O production; and its environmental impact depends on whether its end product is N<sub>2</sub>O or dinitrogen (N<sub>2</sub>) gas. Nitrous oxide is a potent greenhouse gas (GHG), with an atmospheric lifetime of nearly 120 years and a global warming potential 310 times greater than CO<sub>2</sub> (IPCC, 1996b), and is also implicated in the destruction of stratospheric ozone (Crutzen, 1981). Information on the proportion of denitrification gaseous end-products under field conditions is currently lacking. According to Beauchamp (1997), product ratios (N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub>) are as important as the quantities of substrates in determining the proportion of applied N emitted as N<sub>2</sub>O, yet few studies have been devoted to analysis of product ratios. Knowing the proportion of denitrification gaseous end-products is needed in order to establish management strategies that reduce NO<sub>3</sub>-N leaching without simultaneously increasing N<sub>2</sub>O emissions (Elmi, 2002).

With regard to NH<sub>3</sub> volatilisation, Al-Kanani and MacKenzie (1992) reported higher losses with NT than CT. Large NH<sub>3</sub> losses reduce N available for plant uptake, contribute to environmental degradation (i.e. acidification and eutrophication) of natural ecosystems and atmospheric air pollution (FAO, 2001). Moreover, NH<sub>3</sub> can be oxidised and transformed into N<sub>2</sub>O, which constitutes about 5% of the global N<sub>2</sub>O emissions (Ferm, 1998). The IPCC (1996b) estimates that for every kg of NH<sub>3</sub>-N volatilised, approximately 0.01 kg of N<sub>2</sub>O-N is emitted. The fraction of NH<sub>3</sub> that is converted to N<sub>2</sub>O depends on the ecosystem (Weslien et al., 1998). According to Mosier et al. (1996), NH<sub>3</sub> volatilisation from agricultural systems

is globally important, but its influence on N<sub>2</sub>O emissions has not been quantified. These conflicting findings on the impact of tillage on N losses underscore the need for more research. This is particularly important in Atlantic Canada where current information is lacking (Gregorich et al., 2005).

Therefore, the objectives of this study were to: (i) quantify N losses as  $NH_3$  and  $N_2O$  gases and  $NO_3$ -N in the soil profile and drainage water as impacted by tillage following surface application of beef and dairy manure, and (ii) evaluate the impact of tillage on denitrification and ratios of denitrification end-products ( $N_2O:N_2O+N_2$ ) after beef and dairy manure application.

#### 7.2 MATERIALS AND METHODS

### 7.2.1 Experimental Sites and Description

This study was conducted from 2003 through 2005 at two experimental sites. The first site was at Streets Ridge (SR) (45°51′N, 63°40′W) located in Cumberland County, Nova Scotia, Canada. The field measures 5.4 ha with a 4% slope. The soil type is a Queens series (Gleyed Brunisolic Gray Luvisol or Gleyic Luvisol, Canadian and FAO classification), which is a moderately fine textured acid soil developed on neutral and weakly calcareous glacial till of sandy clay loam texture (AAFC, 1998a; Nowland and MacDougall, 1973). Queens soils are imperfectly drained with low hydraulic conductivity and slowly permeable subsoil (Nowland and MacDougall, 1973). A subsurface drainage system was installed in 1988 and consisted of three drain spacings (3,6 and 12 m) at an average depth of 0.8 m. The site was previously used to evaluate the effect of drain spacing on drainage performance (Madani and

Brenton, 1995). It was subsequently modified in 1997 and now there are six plots, each measuring 83 m × 96 m. Since 2002, three of the plots are under CT treatment and the remaining three are under NT treatment. The plots were laid out in a randomised complete block (RCB) design (Appendix 6). Each plot has both subsurface and surface drainage. Buffer drains were installed to hydrologically separate each plot. Drainage water (both surface and subsurface) from each plot flows into a propane heated building, which also houses data collection instruments. Drain discharges were continuously monitored using calibrated tipping buckets connected to a data-logger programmed to record 60 min flow rates year-round. In all there are 12 separate drainage outlets, six for subsurface and six for surface drains.

Manure spreading and most agronomic activities were performed by a co-operating farmer. In the fall 2003 (before manure application) the soil had a pH of 5.7, organic matter content of 3.1% and NO<sub>3</sub><sup>-</sup>N content of 15.2 mg kg<sup>-1</sup>. In late fall (Nov. 3) 2003, semi-solid beef manure was surface applied to each plot at 44 t ha<sup>-1</sup> (168 kg N ha<sup>-1</sup>), while in 2004 manure was applied on Oct. 26 at 50 t ha<sup>-1</sup> (138 kg N ha<sup>-1</sup>) using a tractor drawn manure spreader. Manure on the CT plots was incorporated into the soil (20 cm) using a moldboard plough, while on NT it was left on the surface. Silage corn (DKC 27-15) was planted on May 8, 2004 and June 4, 2005 at 65,000 seeds ha<sup>-1</sup>. In 2004 at planting (spring), all plots were fertilised with diammonium phosphate (DAP) to supply 110 kg N ha<sup>-1</sup>, while in 2005 plots received 140 kg N ha<sup>-1</sup>. Manure characteristics and rates used are shown in Table 7.1.

The second site is at the Bio-Environmental Engineering Centre (BEEC), located at the Nova Scotia Agricultural College (NSAC) in Truro (45°22'N, 63°17'W), Nova Scotia,

Canada. The field is 6.0 ha and has 10 plots each measuring 36 × 72 m separated by buffer drains. Since 2002, five of the plots are under CT while the remaining five are under NT (Appendix 7). Each plot has 100 mm subsurface drains placed at a depth of 0.8 m with a 12 m spacing. Drainage water from each plot flows into two outlet buildings, each equipped with data collection instruments. Drain discharges were continuously monitored (year-round) using calibrated tipping buckets connected to a data-logger. The dominant soil types are Pugwash (Humo-Ferric Podzol or Orthic Podzol, Canadian and FAO classification) and Debert series (Gleyed Degraded Dystric Brunosol or Dystric Cambisol, Canadian and FAO classification). Webb et al. (1991) provided detailed characteristics of these soil series.

Liquid dairy manure application and all agronomic activities were performed by the NSAC farm staff. In the spring of 2004 (before dairy manure application) the soil had a pH of 6.2, organic matter content of 2.8% and NO<sub>3</sub><sup>-</sup>-N content of 6.2 mg kg<sup>-1</sup>. In 2004 (spring), liquid dairy manure was surface applied to each plot on May 21 at 25 t ha<sup>-1</sup> (63 kg N ha<sup>-1</sup>), while in 2005 (spring) it was applied on May 11 at 65 t ha<sup>-1</sup> (159 kg N ha<sup>-1</sup>) using a tractor drawn manure spreader. On the CT plots, a moldboard plough was used to incorporate the manure to a depth of about 20 cm immediately after application, while for the NT manure remained on the surface. In 2004 all plots were seeded to soybeans (DKB 00/99) at 75 kg seeds ha<sup>-1</sup> on May 27. In 2005 plots were seeded to barley (AC Mapple) on May 16 at 135 kg seeds ha<sup>-1</sup>. Inorganic fertiliser was not applied to the plots in either year. Manure characteristics and application rates used are shown in Table 7.1.

#### 7.2.2 Ammonia Measurements

At both sites, NH<sub>3</sub> emissions were monitored using static acid traps made out of plexiglass (Appendix 2a). The traps measured 40 cm (height) × 20 cm (length) × 20 cm (width) placed randomly in the plots soon after manure spreading. The traps were inserted into the soil to a depth of about 1 to 2 cm to prevent NH<sub>3</sub> leakage between the soil and the traps. Absorber foam measuring 20.5 cm (length)  $\times$  20.5 cm (width)  $\times$  2.5 cm (thickness) was immersed in a glycerol-phosphoric acid solution prepared from 50 mL L<sup>-1</sup> glycerol and 50 mL L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> (Kunelius et al., 1987; Gordon et al, 2000). The foam absorbers were made to fit tightly into the traps to reduce NH<sub>3</sub> leakage between the trap and foam. Two foam absorbers per trap were used; one at the bottom (30 cm) above the soil to trap NH<sub>3</sub> volatilised from the soil, and the upper one at the top of the chamber protecting the bottom absorber from atmospheric NH<sub>3</sub>. The traps had a triangular plexiglass on top, which protected the absorbers from rainfall but allowed free air movement. After 1, 2, 4, 7 and 10 d following manure spreading, the foam absorbers were removed from the traps and placed in freezer bags, which were immediately sealed and subsequently put in large plastic bags. The top absorber foam from each trap was discarded while the bottom absorber was thoroughly rinsed in 250 mL 2M KCl to extract the trapped NH<sub>3</sub> (Kunelius et al., 1987). The solution was decanted into vials and kept frozen until analysis using a Technicon auto-analyser (Technicon Instruments, Tarrytown, NY) following the method recommended Keeney and Nelson (1982). Total NH<sub>3</sub> losses (kg ha<sup>-1</sup>) were calculated on the basis of the soil surface area (0.04) m<sup>2</sup>) covered by the traps.

## 7.2.3 Denitrification and N<sub>2</sub>O Measurements

Denitrification and N<sub>2</sub>O production rates were measured using the core incubation method, in the presence and absence of acetylene (C<sub>2</sub>H<sub>2</sub>) gas, respectively (Yoshinari et al, 1977). Acetylene was produced by dissolving calcium carbide (CaC<sub>2</sub>) in water. Two minimally disturbed soil core samples from each plot were extracted using aluminium cylinders 5.0 cm (inner diameter) × 15 cm (length). The cylinders were perforated along the sides to enhance C<sub>2</sub>H<sub>2</sub> diffusion. The soil core samples were placed in 1.5 L Mason jars fitted with a rubber septum for gas sampling and incubated for 24 h outdoors in a 22 cm deep hole. For denitrification measurements, 75 mL head space air was replaced by acetylene (5% v/v) to inhibit N<sub>2</sub>O reduction to N<sub>2</sub> (Yoshinari et al, 1977). The second sample was incubated without C<sub>2</sub>H<sub>2</sub> to estimate N<sub>2</sub>O emissions. Prior to gas sampling, the head space was thoroughly mixed by inserting a syringe through the rubber septum and pumping several times. The gas samples were transferred into pre-evacuated 12 mL glass vials (Labco Exetainer, High Wycombe UK) and maintained until analysis using a Varian GP3800 gas chromatograph (GC) fitted with an electron capture detector (Varian Inc., Palo Alto, CA, USA). The N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratios were calculated using the following (Elmi et al., 2003):

$$\frac{(N_2O - N)without C_2H_2}{(N_2O - N)with C_2H_2} = \frac{N_2O}{N_2O + N_2}$$
(1)

## 7.2.4 Nitrate-N Measurements in the Soil Profile

At each experimental site, soil samples for NO<sub>3</sub><sup>-</sup>-N analysis were collected prior to planting (April or May) and shortly after harvest (September or October) at 0-20 cm, 20-40

cm, and 40-60 cm depths using a hand-held auger sampling probe. Samples were analysed for NO<sub>3</sub><sup>-</sup>-N by the Nova Scotia Department of Agriculture and Fisheries Laboratory using a nitrate electrode (Keeney and Nelson, 1982). In addition, soil samples (0-15 cm) from each plot were collected for NO<sub>3</sub><sup>-</sup>-N and NH<sub>4</sub><sup>+</sup>-N determination in conjunction with denitrification measurements. These samples were air-dried and 5 g sub-samples were extracted with 50 mL 2M KCl and filtered through Whatman No. 42 filter paper (Maynard and Kalra, 1993). The extracts were kept frozen until analysis using a Technicon auto-analyser (Technicon Instruments, Tarrytown, NY) following the method recommended by Keeney and Nelson (1982). The detection limits for NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N were 0.03 and 0.05 mg L <sup>-1</sup>, respectively. Soil water content and bulk density at each sampling date were determined by oven-drying soil cores at 105°C for 48 h. Percent water filled pore space (%WFPS) was determined as follows:

$$\%WFPS = (\theta_v / P_t) \times 100 \tag{2}$$

where  $P_t$  is the total porosity calculated assuming particle density of 2.65 Mg m<sup>-3</sup> and  $\theta_v$  is volumetric soil water content.

# 7.2.5 Drainage Water Samples Collection and Analysis

Drainage water samples for NO<sub>3</sub>-N and other nutrients analysis at both sites and from each plot were collected from the drainage water using Isco 6700 auto-samplers (Isco, Lincoln, NE) and poured into 50 mL centrifuge tubes. Water samples were kept at 4°C until analysis using a Waters Ion Chromatography System (Waters Canada LTD., Dorval, PQ). Sampling was performed according to a flow-weighted average strategy. The frequency of

water sampling dependent on the duration of each flow event. Data from each drain flow event and NO<sub>3</sub><sup>-</sup>-N concentrations were used to calculate the flow-weighted average. Nitrate-N load was calculated by multiplying the flow volume with NO<sub>3</sub><sup>-</sup>-N concentration in the drainage water. The annual load (kg N ha<sup>-1</sup>) was calculated by adding all individual event loads and dividing by cumulative flow volume, and subsequently dividing by the area of the plot.

### 7.2.6 Statistical Analysis

All data were subjected to analysis of variance (ANOVA) using the PROC GLM in SAS (SAS Institute, 1996). With regard to denitrification rates and  $N_2O$  fluxes, data for each sampling day were analysed separately. Unless otherwise mentioned, differences among treatments were declared to be significant at p < 0.05. Due to high variability and violation of the normality and constant variance assumptions, denitrification and  $N_2O$  data were log-transformed before analysis.

#### 7.3 RESULTS AND DISCUSSION

### 7.3.1 Climatic Conditions

The mean monthly temperature and total precipitation at both sites (SR and BEEC) during both seasons (2003/04 and 2004/05) are provided in Tables 7.2a, b. During the 2003/04 season, the total precipitation at SR was near average. However, in November (2003), May and July (2004) the precipitation was 50, 22 and 49% below average, respectively, while in October (2003) and April (2004), it was 27 and 61% above average,

respectively. During the 2004/05 season, in August and September (2004) the precipitation was 73 and 71% below normal, respectively, while in November (2004) and May (2005), it was 20 and 56% above normal, respectively. At BEEC meanwhile, total seasonal (April-October) precipitation in 2004 was 7% below normal, while in 2005 it was 33% above normal. May and July were the driest months in 2004, receiving less than 50% of normal precipitation. In June and August 2005, the precipitation received was 32 and 41% below normal, respectively, while in September and October, it was 48 and 167% above normal, respectively. Temperature at both sites and both seasons was near normal.

#### 7.3.2 Ammonia Volatilisation

Ammonia volatilisation was significantly (p< 0.05) affected by tillage at both sites during both seasons with NT having higher NH<sub>3</sub> emissions (Table 7.3). During 2003/2004 at SR, 0.29 and 3.36 kg N ha<sup>-1</sup> were lost through NH<sub>3</sub> volatilisation from the CT and NT plots, respectively. In 2004/2005, the losses were 2.60 kg N ha<sup>-1</sup> for CT and 13.65 kg N ha<sup>-1</sup> for NT. Meanwhile, at BEEC in 2004, 1.64 and 5.82 kg N ha<sup>-1</sup> were lost through NH<sub>3</sub> volatilisation from the CT and NT plots, respectively. In 2005 the losses were 3.37 kg N ha<sup>-1</sup> for CT and 20.14 kg N ha<sup>-1</sup> for NT. The lower NH<sub>3</sub> emissions from CT at both sites is attributed to the fact that manure was incorporated into the soil soon after spreading. These results are consistent with previous studies which have shown that incorporation of manure soon after spreading can reduce NH<sub>3</sub> volatilisation by as much as 90% (Sommer and Hutchings, 1995; Malgeryd, 1998). In 2003/2004, incorporation reduced NH<sub>3</sub> emissions by

91% at SR and by 72% at BEEC. In 2004/2005 NH $_3$  losses were reduced by 81% at SR and 83% at BEEC.

## 7.3.3 Denitrification Rates and N2O Emissions

Daily denitrification and N<sub>2</sub>O fluxes from both sites and seasons are shown in Figures 7.1 through 7.4. They followed a similar trend, regardless of the tillage system. During both years, denitrification and N<sub>2</sub>O emissions under NT were generally higher for both sites; although during most sampling dates, the difference was not significant. This is consistent with Fan et al. (1997) who reported greater denitrification rates under NT in a corn field in Quebec. They concluded that to reduce N<sub>2</sub>O emissions, corn production should be carried out under CT. Similar findings were also reported by Staley et al. (1990) and Palma et al. (1997) who attributed the greater denitrification and N<sub>2</sub>O production under NT in part due to the presence of higher amounts of available C under NT and greater aeration under CT created by tillage. On the contrary, Malhi et al (2006) reported lower N<sub>2</sub>O emissions from NT in a field under cereal and oilseeds in Saskatchewan. In Ontario, Drury et al. (2006) reported that N<sub>2</sub>O losses under NT were on average 23% lower than in CT. Meanwhile, Elmi et al. (2003) reported that denitrification and N<sub>2</sub>O fluxes under NT were similar to or slightly higher than in CT for a corn field in Quebec. Groffman (1984) reported no difference on denitrification activity between NT and CT when soil water content was high, but when soil water content was low, denitrification activity was higher under NT. denitrification and  $N_2O$  fluxes under NT in this study may be attributed to higher (p< 0.05) %WFPS under NT during most sampling dates (Figures 7.5 and 7.6).

During most sampling dates,  $N_2O$  fluxes were smaller than denitrification rates implying that  $N_2$  formed a large proportion of the denitrification gaseous end-products, irrespective of tillage system (Figures 7.1 to 7.4). However, during a few sampling dates, particularly under CT, daily  $N_2O$  fluxes were higher than denitrification rates indicating that nitrification might have contributed to  $N_2O$  production. This may be attributed to conditions of greater oxygen supply under CT created by ploughing and lower %WFPS. Soil water content affects oxygen supply into the soil and thus denitrification. On several occasions the soil water content under CT at both sites during the 2003/2004 season fell below 60% WFPS (Figures 7.5 and 7.6), a value regarded as the threshold for denitrification (Granli and Bøckman, 1994; Linn and Doran, 1984; Weier et al., 1993). Regression analysis showed that  $N_2O$  fluxes were significantly (p<0.001 to 0.005,  $R^2$ =0.24 to 0.93) positively correlated with denitrification at both sites and both years (data not shown). This finding indicates that most of the  $N_2O$  was produced through denitrification.

The average daily denitrification rates over a 2-year sampling period at SR ranged from 211 to 264 g N ha<sup>-1</sup> d<sup>-1</sup> for NT and 88 to 153 g N ha<sup>-1</sup> d<sup>-1</sup> for CT (Table 7.3). Meanwhile, the average daily N<sub>2</sub>O fluxes ranged from 109 to 119 g N ha<sup>-1</sup> d<sup>-1</sup> for NT and 43 to 81 g N ha<sup>-1</sup> d<sup>-1</sup> for CT. At BEEC, average daily denitrification rates ranged from 107 to 121 g N ha<sup>-1</sup> d<sup>-1</sup> for NT and 52 to 90 g N ha<sup>-1</sup> d<sup>-1</sup> for CT (Table 7.3). The average N<sub>2</sub>O fluxes for BEEC ranged from 39 to 66 and 26 to 28 g N ha<sup>-1</sup> d<sup>-1</sup> for NT and CT, respectively. Paul and Zebarth (1997) reported average daily denitrification rates of 338 g N ha<sup>-1</sup> d<sup>-1</sup> on manured plots and 107 g N ha<sup>-1</sup> d<sup>-1</sup> on non-manured plots, after applying dairy cattle slurry at 600 kg N ha<sup>-1</sup>. Similarly, Lowrance et al. (1998) reported denitrification rates ranging

from 20 to 246 g N ha<sup>-1</sup> d<sup>-1</sup>after applying liquid dairy manure at rates ranging from 246 to 802 kg N ha<sup>-1</sup>. Thompson and Meisinger (2004) observed average denitrification rates ranging from 90 to 200 g N ha<sup>-1</sup> d<sup>-1</sup> and 90 to 320 g N ha<sup>-1</sup> d<sup>-1</sup> for surface applied and incorporated cattle slurry, respectively. They further reported that highest denitrification rates were 340 and 700 g N ha<sup>-1</sup> d<sup>-1</sup> for surface applied and incorporated cattle slurry, respectively. In Quebec, however, Elmi et al. (2003) recorded seasonal average N<sub>2</sub>O fluxes ranging from 6 to 27 g N ha<sup>-1</sup> d<sup>-1</sup> for NT and 9 to 20 g N ha<sup>-1</sup> d<sup>-1</sup> for CT after application of 140 kg N ha<sup>-1</sup> inorganic fertiliser. The higher values in the current study may be attributed to higher soil WFPS (Figures 7.5 and 7.6) compared to the Quebec study where the average seasonal WFPS was below 60%, and the different fertilisers used (i.e., manure versus inorganic fertilisers).

Linear regression results between %WFPS and daily denitrification and  $N_2O$  fluxes are presented in Table 7.4. In 2003/2004 at SR, both denitrification and  $N_2O$  fluxes were poorly correlated with WFPS, reiterating observations made by Thompson and Meisinger (2004). However, in 2004/2005 both denitrification and  $N_2O$  fluxes correlated significantly (p< 0.05) with WFPS, but accounted for only 35% of the variance (Table 7.4). At BEEC, in both years denitrification and  $N_2O$  fluxes correlated significantly (p< 0.05) with WFPS, but accounted for only 28 and 48% of the variance (Table 7.4). This finding supports the observation that denitrification and  $N_2O$  emissions are impacted by WFPS, with greater emissions observed at higher WFPS (Linn and Doran, 1984; Weier et al., 1993).

Soil NO<sub>3</sub>-N contents in the (0-15 cm) were not affected by tillage at both sites, in both years, and showed no clear trend of increase or decline over time (data not shown).

Regression analysis showed that there was a significant (p<0.05) positive linear relationship between both denitrification and  $N_2O$  fluxes and soil  $NO_3$ -N (0-15 cm) at BEEC during both years (Table 7.4). Generally, both denitrification and  $N_2O$  fluxes increased with an increase in soil  $NO_3$ -N, in line with previous observations (Granli and Bøckman, 1994). The relationship at SR was in most cases poor, although in 2004/2005 a marginally significant (p = 0.05) positive linear relationship between  $NO_3$ -N and  $N_2O$  fluxes was observed (Table 7.4). Elmi (2002) found poor correlation between denitrification and soil  $NO_3$ -N in a corn field in Quebec, after application of inorganic N fertiliser. Similarly, Lowrance et al (1998) and Thompson and Meisinger (2004) found poor correlation between denitrification and soil  $NO_3$ -N after applying liquid cattle manure to forage and no-till maize fields, respectively.

# 7.3.4 Ratios of N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub>

The impact of denitrification on the environment depends on whether the end-product is N<sub>2</sub>O or N<sub>2</sub>. The seasonal average N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratios for both sites were significantly (p< 0.05) affected by tillage (Table 7.3). In general, NT had lower (p< 0.05) N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratios compared to CT in both seasons and both sites. The only exception was at BEEC in 2004/2005 when the ratio was not significantly different. This result indicates that under NT, there was more complete reduction of N<sub>2</sub>O to N<sub>2</sub>, in part due to higher soil water content under NT (Weier et al., 1993). During 2003/2004 the average N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratios at SR were 0.8 for NT and 1.2 for CT, while in the 2004/2005 season they were 0.7 for NT and 0.9 for CT. At BEEC, the values were 0.5 for NT and 1.1 for CT in 2003/2004, and 0.6 and 0.5 for NT and CT, respectively, in 2004/2005. Results from this study concur with Elmi et

al. (2003) who reported lower  $N_2O:N_2O+N_2$  ratios under NT in a study conducted in corn field in Quebec. They reported  $N_2O:N_2O+N_2$  ratios of 0.60 and 0.41 for NT and 1.0 and 0.38 for CT during the 1999 and 2000 cropping seasons, respectively. Lowrance et al. (1998) reported an average  $N_2O:N_2O+N_2$  ratio of 0.4 after applying liquid dairy manure to forage. Meanwhile, in a laboratory experiment, Webster and Hopkins (1996) recorded  $N_2O:N_2O+N_2$  ratios of 0.50, and 0.18 to 0.21 for a drier and wetter soil, respectively.

During 2003/2004 at both sites the  $N_2O:N_2O+N_2$  ratios for CT were > 1.0, indicating that the nitrification process might have contributed to  $N_2O$  production in the soil cores incubated without  $C_2H_2$  (Elmi et al., 2003; Weier et al., 1993). This might have been due to better aeration created by ploughing and/or lower WFPS under CT (Figures 7.5 and 7.6). Ploughing increases aeration, enhance evaporation and speeds-up crop residue degradation by soil microbes. The average %WFPS at both sites during 2003/2004 was lower (p<0.05) under CT (Table 7.3). At SR the average WFPS was 76% for NT and 66% for CT, while at BEEC it was 76% for NT and 60% for CT. Maximum  $N_2O$  emissions occur at WFPS where both nitrification and denitrification can proceed, which is normally between 45 and 75% (Granli and Bøckman, 1994). Soils close to saturation show high denitrification activity but low  $N_2O$  emission, because when oxygen is limiting denitrifiers consume more  $N_2O$  than under aerobic conditions (FAO, 2001).

## 7.3.5 Nitrate-N in the Soil Profile

When averaged across all soil depths,  $NO_3^-$ -N was significantly (p < 0.05) higher in CT than NT. In general,  $NO_3^-$ -N decreased with depth in both fields and tillage systems. The only

exception was for BEEC in the fall 2004 and spring 2005 when NO<sub>3</sub><sup>-</sup>-N for the 20-40 cm soil depth under CT was higher than in the 0-20 cm depth (Figures 7.7 and 7.8). This may have been due to the fact that the moldboard ploughing during field preparation and manure incorporation led to manure and plant residues accumulating in the 20-40 cm depth. Alternatively, there might have been some NO<sub>3</sub><sup>-</sup>-N movement from the top layer to the 20-40 cm layer. In most cases, NO<sub>3</sub><sup>-</sup>-N was significantly higher under CT for all soil depths. Interestingly, at SR in fall 2004, the NO<sub>3</sub><sup>-</sup>-N concentration was similar for both tillage systems for all the soil depths. However, in spring 2005, the NO<sub>3</sub><sup>-</sup>-N was slightly higher under NT at the 0-20 cm layer, although the difference was not significant (p>0.05). In the fall 2005, the NO<sub>3</sub><sup>-</sup>-N concentration was significantly (p< 0.05) higher under NT at the 0-20 cm layer but similar in the other layers. The lower NO<sub>3</sub><sup>-</sup>-N under NT confirms previous findings reported by Elmi et al. (2003) and Randall and Iragavara (1995). This may be attributed to higher denitrification rates in the NT plots.

Another factor that may have contributed to the lower NO<sub>3</sub><sup>-</sup>-N under NT could have been the higher NH<sub>3</sub> losses through volatilisation under NT reducing the N pool available for nitrification. As previously discussed, NH<sub>3</sub> volatilisation was significantly (p< 0.05) higher under NT for both sites and seasons. In addition, higher rates of mineralisation under CT may have increased the N pool available for nitrification, particularly in the 0-20 cm depth. It is well known that ploughing and cultivation increase crop residue degradation by soil microbes. Halvorson et al. (2001) reported higher NO<sub>3</sub><sup>-</sup>-N levels in the top 150 cm of the soil under CT and attributed this to increased N mineralisation caused by cultivation. Under NT more N can

be tied up in organic matter and crop residues thus resulting in lower soil NO<sub>3</sub><sup>-</sup>-N concentration (Halvorson et al., 2001).

In 2004/2005, at SR in most cases, soil NO<sub>3</sub>-N concentrations in the soil profile were either similar or slightly higher under NT than CT. This can be explained by the fact that average seasonal daily denitrification and N<sub>2</sub>O fluxes and total N losses due to denitrification were similar for both tillage systems (Table 7.3). This finding further confirms the observation that higher denitrification under NT is responsible for the lower soil NO<sub>3</sub>-N relative to CT.

## 7.3.6 Nitrate-N Concentration in Drainage Water

Annual drainage flow volumes, NO<sub>3</sub><sup>-</sup>-N concentrations and NO<sub>3</sub><sup>-</sup>-N loads for SR and BEEC are shown in Tables 7.5 and 7.6, respectively. At both sites during both seasons, the annual drainage flow volumes were not affected by tillage system (p> 0.05), although at BEEC, drainage volumes were 1.8 and 2.1 times greater in NT during 2003/2004 and 2004/2005, respectively. Endale et al. (2002) and Patni et al. (1996) observed higher drainage volume under NT than CT and attributed this to preferential flow due to macropores, reduced surface runoff due to crop residue, higher infiltration and lower evapotranspiration under NT.

At SR, NO<sub>3</sub>-N concentrations in subsurface drainage water were 35 and 19% lower in NT than CT during 2003/2004 and 2004/2005, respectively. The differences however, were not significant (p> 0.05). For surface drainage water, during 2003/2004, higher (p< 0.05) NO<sub>3</sub>-N concentrations in CT than NT were observed, while in 2004/2005 the reverse

was observed (Table 7.5). At BEEC, during both seasons, NO<sub>3</sub><sup>-</sup>-N concentrations in drainage water were higher (p< 0.05) under CT compared to NT (Table 7.6). From the same sites used for the current study, Thiagarajan (2005) reported lower NO<sub>3</sub><sup>-</sup>-N concentrations in drainage water under NT compared to CT during 2002/2003 and 2003/2004 seasons. Patni et al. (1998) observed consistently higher average NO<sub>3</sub><sup>-</sup>-N concentrations in drainage water under CT than NT, however, the difference was not significant. Stoddard et al. (2005) found that tillage system had no significant impact on NO<sub>3</sub><sup>-</sup>-N concentrations in leachate, when comparing NT and chisel ploughing plus secondary discing. They attributed this to the fact that, chisel ploughing plus discing did not substantially disturb soil physical and microbial characteristics. The generally lower NO<sub>3</sub><sup>-</sup>-N concentrations in drainage water under NT relative to CT in the current study, may be partially attributed to the higher denitrification rates observed under NT.

Annual NO<sub>3</sub><sup>-</sup>-N loads for subsurface drainage water at SR were not affected by tillage system (p> 0.05) during both seasons. However, NO<sub>3</sub><sup>-</sup>-N loads for surface drainage water were only affected by tillage during 2003/2004, with higher loads coming from CT plots (Table 7.4). The higher NO<sub>3</sub><sup>-</sup>-N loads in CT during 2003/04 were a result of higher NO<sub>3</sub><sup>-</sup>-N concentrations in drainage water in CT coupled with higher denitrification losses in NT. At BEEC during both seasons, the NO<sub>3</sub><sup>-</sup>-N loads from NT and CT were not significantly different (Table 7.5). Results of the current study therefore, suggest that NT can be used to reduce NO<sub>3</sub><sup>-</sup>-N leaching to groundwater, albeit with trade-offs.

## 7.4 CONCLUSIONS

Tillage had a significant effect on NH<sub>3</sub> volatilisation with higher NH<sub>3</sub> losses from NT. In addition, significantly greater denitrification rates and higher N<sub>2</sub>O emissions were observed from NT, particularly during the 2003/2004 season. Conversely, generally lower N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratios were observed under NT suggesting more complete reduction of N<sub>2</sub>O to N<sub>2</sub>. Both denitrification and N<sub>2</sub>O emissions increased with higher %WFPS and soil NO<sub>3</sub><sup>-</sup>-N contents (0-15 cm). Lower soil and tile drainage water NO<sub>3</sub><sup>-</sup>-N concentrations were observed under NT indicating enhanced denitrification rates removed NO<sub>3</sub><sup>-</sup>-N. Consequently, NT may be a viable strategy to remove NO<sub>3</sub><sup>-</sup>-N from the soil and thus reduce surface and groundwater contamination. However, it should be noted that the use of NT to reduce NO<sub>3</sub><sup>-</sup>-N leaching may actually simultaneously increase NH<sub>3</sub> and N<sub>2</sub>O emissions, thus creating a tradeoff among the different N species. Therefore, mitigation strategies for these pollutants should consider the whole N cycle simultaneously within the agricultural ecosystem.

**Table 7.1.** Manure characteristics and application rates used at Streets Ridge (SR) and Bio-Environmental Engineering Centre (BEEC).

Season							
	рН	pH Dry Matter (%)	Total N (%)	Ammonium (%)	Manure applied (t ha <sup>-1</sup> )	Total N applied (kg ha <sup>-1</sup> )	Total NH <sub>4</sub> <sup>+</sup> -N applied (kg ha <sup>-1</sup> )
			S	SR (Semi Solid Beef Manure)	3eef Manure)		
Fall 2003/04	7.7	23.8	0.38	0.05	44.0	168.3	22.8
Fall 2004/05	8.0	11.2	0.28	0.03	50.0	137.6	16.5
			B	BEEC (Liquid Dairy Manure)	airy Manure)		
Spring 2004	7.5	6.3	0.25	0.13	25.0	62.5	33.5
	6.9	10.6	0.24	0.11	65.0	158.6	72.8

**Table 7.2a.** Mean monthly air temperature and precipitation for Streets Ridge (SR) during 2003/2004 and 2004/05 seasons and the long-term (30 yr; 1970-2000) average. All data for SR were recorded at the Nappan Climate Station (Environment Canada, 2006)

	Air 7	Temperatu	re (°C)	Pre	cipitation (	mm)
Month	2003/04	2004/05	Normal	2003/04	2004/05	Normal
October	9.6	9.5	8.2	120.8	114.6	95.3
November	4.3	2.5	2.7	52.7	110.8	106.0
April	4.2	5.6	3.8	143.1	74.7	88.4
May	9.8	8.7	10.0	46.3	92.4	59.1
June	13.3	15.4	15.0	99.3	88.1	90.0
July	18.5	18.0	18.4	50.7	67.3	83.1
August	18.7	18.6	17.9	87.8	26.2	98.5
September	13.5	15.4	13.7	69.2	138.0	80.9
Mean/Total	11.5	11.7	11.2	669.9	712.1	701.3

**Table 7.2b.** Mean monthly air temperature and precipitation for Bio-Environmental Engineering Centre (BEEC) during 2004 and 2005 seasons and the long-term (30 yr; 1970-2000) average. Long-term average data for BEEC were taken from the Truro Climate Station (Environment Canada, 2006)

	Air	Tempera	ture (°C)	Pr	ecipitation	(mm)
Month	2004	2005	Normal	2004	2005	Normal
April	4.5	4.8	3.9	108.9	121.2	96.1
May	8.8	8.6	9.8	39.9	115.3	85.1
June	13.1	15.3	14.7	74.2	60.8	89.8
July	18.7	18.5	18.4	37.6	100.2	85.4
August	18.8	18.6	17.8	124.2	59.5	101.3
September	13.3	15.4	13.4	116.9	155.0	104.6
October	9.6	10.3	7.7	115.1	269.9	101.1
Mean/Total	12.4	13.1	12.2	616.7	881.9	663.4

seasonal denitrification rates and N2O fluxes, and average seasonal water-filled pore space (%WFPS) at 0-15 cm depth during Table 7.3. Impact of no-tillage (NT) and conventional tillage (CT) on NH<sub>3</sub> loss, average seasonal N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratios, average 2003/2004 and 2004/2005 at Streets Ridge (SR) and Bio-Environmental Engineering Centre (BEEC).

Season	Tillage	NH <sub>3</sub> (kg N ha <sup>-1</sup> )	$N_2O:N_2O+N_2$ Ratio	Average Denitrification Rates (g N ha <sup>-1</sup> d <sup>-1</sup> )	Average $N_2O$ Flux (g N ha <sup>-1</sup> d <sup>-1</sup> )	Average WFPS (%)
				SR		
2003/04	NT	3.4 a	0.76 b	263.6 a	119.4 a	76.1 a
	CT	0.3 b	1.20 a	87.9 b	43.3 b	9 0.99
2004/05	Z	13.7 a	0.65 b	210.6 a	108.8 a	78.5 a
	CT	2.6 b	0.94 a	153.1 a	80.6 a	79.9 a
				BEEC		
2004	Z	5.88	0.50 b	121.3 a	38.6 a	75.8 a
• • •	CT	1.6 b	1.10 a	52.3 b	26.4 a	59.6 b
2005	IN	20.1 a	0.59 a	107.0 a	65.7 a	81.1 a
; ;	CT	3.4 b	0.48 a	90.0 a	28.1 b	70.3 b

Means followed by the same letter within the same column and each season or year are not significantly different (p> 0.05).

**Table 7.4.** Linear regression results between water-filled pore space (%WFPS) and  $NO_3$ -N (0-15 cm) and daily denitrification rates and  $N_2O$  fluxes during 2003/2004 and 2004/2005 at Streets Ridge (SR) and Bio-Environmental Engineering Centre (BEEC). (Note, NT and CT denitrification,  $N_2O$  and %WFPS and  $NO_3$ -N data were pooled for each year).

Year	Predictor	Denitrifica	tion rates	N <sub>2</sub> C	O flux
	variable	R <sup>2</sup>	P-value	$\mathbf{R}^2$	P-value
			SR		
2003/2004	%WFPS	0.04	0.25	0.04	0.27
	$NO_3$ -N	0.07	0.34	0.20	0.11
	Combined*	0.25	0.21	0.37	0.08
2004/2005	%WFPS	0.43	<0.01*	0.50	<0.01*
2001,200	NO <sub>3</sub> -N	0.03	0.34	0.12	0.05
	Combined*	0.44	<0.01*	0.63	<0.01*
		В	EEC		
2004	%WFPS	0.28	0.02*	0.23	0.04*
	NO <sub>3</sub> -N	0.38	0.01*	0.37	0.01*
	Combined*	0.52	<0.01*	0.48	<0.01*
2005	%WFPS	0.28	0.04*	0.23	0.08
_ ; <del></del>	$NO_3$ -N	0.72	<0.01*	0.41	0.01*
	Combined*	0.73	<0.01*	0.44	0.04*

<sup>•</sup> Combined %WFPS and NO<sub>3</sub>-N (multiple regression)

<sup>\*</sup> Significant at p< 0.05

**Table 7.5.** Impact of no-tillage (NT) and conventional tillage (CT) on annual drainage flow volume, annual flow weighted average nitrate-N ( $NO_3^--N$ ) concentration ( $mg L^{-1}$ ) and annual  $NO_3^--N$  load ( $kg ha^{-1}$ ) during 2003/2004 and 2004/2005 from subsurface and surface drainage at Streets Ridge (SR).

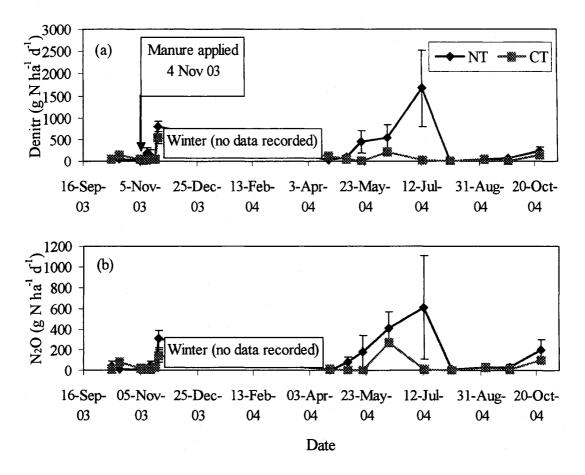
			Subsurface			Surface	<i>2</i>
Season	Tillage	Flow (mm)	NO <sub>3</sub> -N (mg L <sup>-1</sup> )	Load (kg ha <sup>-1</sup> )	Flow (mm)	NO <sub>3</sub> -N (mg L <sup>-1</sup> )	Load (kg ha <sup>-1</sup> )
2003/2004	NT	250 a	2.83 a	7.10 a	213 a	1.02 b	2.15 b
	CT	242 a	4.34 a	9.33 a	209 a	2.61 a	5.13 a
2004/2005	NT	365 a	2.50 a	17.05 a	182 a	4.65 a	4.61 a
	CT	277 a	3.10 a	10.91 a	232 a	3.91 b	7.17 a

Means followed by the same letter within the same column and each season or year are not significantly different (p> 0.05).

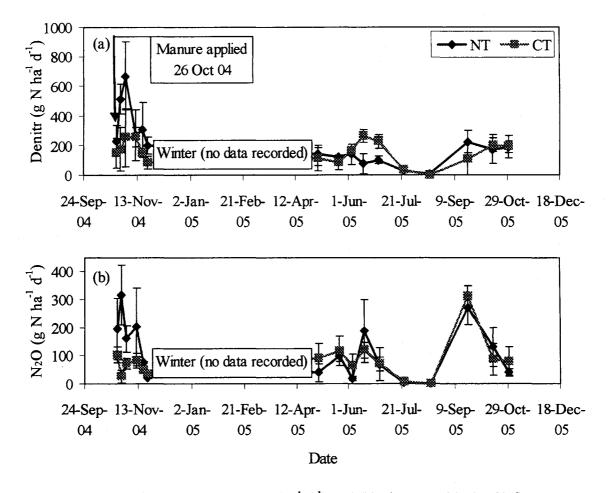
**Table 7.6.** Impact of no-tillage (NT) and conventional tillage (CT) on annual drainage flow volume, annual flow weighted average nitrate-N (NO<sub>3</sub><sup>-</sup>-N) concentration (mg L<sup>-1</sup>) and annual NO<sub>3</sub><sup>-</sup>-N load (kg ha<sup>-1</sup>) during 2003/2004 and 2004/2005 at Bio-Environmental Engineering Centre (BEEC).

Season	Tillage	Flow (mm)	NO <sub>3</sub> N (mg L <sup>-1</sup> )	Load (kg ha <sup>-1</sup> )
2003/2004	NT	314 a	5.17 b	14.57 a
	CT	173 a	7.03 a	11.72 a
2004/2005	NT	335 a	6.91 b	22.37 a
	CT	157 a	10.54 a	18.19 a

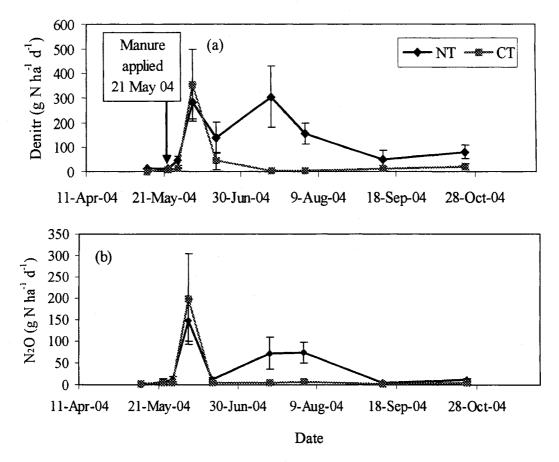
Means followed by the same letter within the same column and each season or year are not significantly different (p > 0.05).



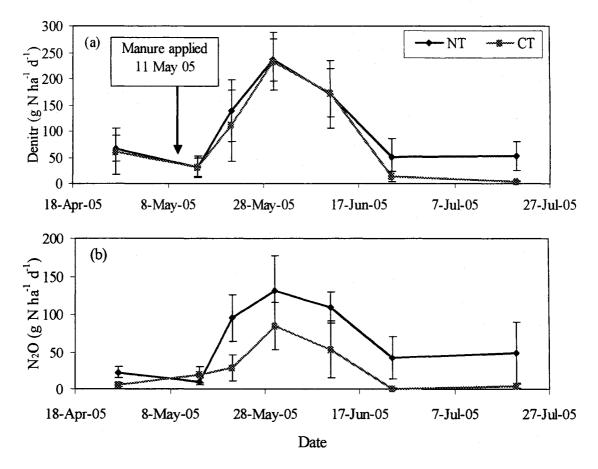
**Figure 7.1.** (a) Denitrification rates (g N ha<sup>-1</sup> d<sup>-1</sup>) and (b) nitrous oxide (N<sub>2</sub>O) fluxes (g N ha<sup>-1</sup> d<sup>-1</sup>) under no-tillage (NT) and conventional tillage (CT) systems at Streets Ridge, Nova Scotia in 2003/2004. Vertical bars indicate standard error of the mean (n = 3).



**Figure 7.2.** (a) Denitrification rates (g N ha<sup>-1</sup> d<sup>-1</sup>) and (b) nitrous oxide (N<sub>2</sub>O) fluxes (g N ha<sup>-1</sup> d<sup>-1</sup>) under no-tillage (NT) and conventional tillage (CT) systems at Streets Ridge, Nova Scotia in 2004/2005. Vertical bars indicate standard error of the mean (n = 3).



**Figure 7.3.** (a) Denitrification rates (g N ha<sup>-1</sup> d<sup>-1</sup>) and (b) nitrous oxide ( $N_2O$ ) fluxes (g N ha<sup>-1</sup> d<sup>-1</sup>) under no-tillage (NT) and conventional tillage (CT) systems at Bio-Environmental Engineering Centre, Truro, Nova Scotia in 2004. Vertical bars indicate standard error of the mean (n = 5).



**Figure 7.4.** (a) Denitrification rates (g N ha<sup>-1</sup> d<sup>-1</sup>) and (b) nitrous oxide (N<sub>2</sub>O) fluxes (g N ha<sup>-1</sup> d<sup>-1</sup>) under no-tillage (NT) and conventional tillage (CT) systems at Bio-Environmental Engineering Centre, Truro, Nova Scotia in 2005. Vertical bars indicate standard error of the mean (n = 5).

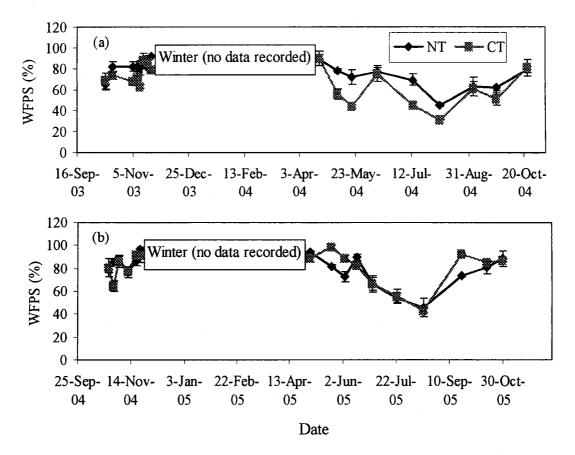


Figure 7.5. Water filled pore space percentage (%WFPS) under no-tillage (NT) and conventional tillage (CT) systems at Streets Ridge, Nova Scotia during (a) 2003/2004 and (b) 2004/2005 seasons. Vertical bars indicate standard error of the mean (n = 3).

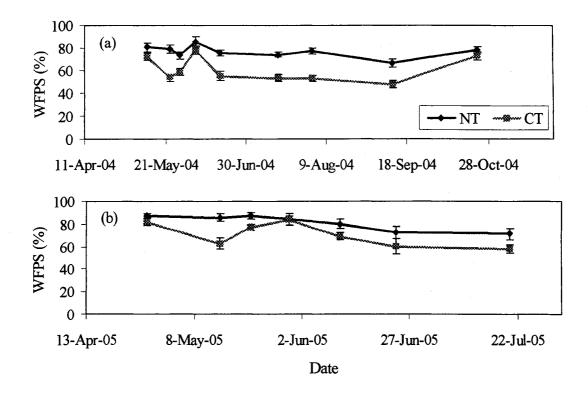


Figure 7.6. Water filled pore space percentage (%WFPS) under no-tillage (NT) and conventional tillage (CT) systems at Bio-Environmental Engineering Centre, Truro, Nova Scotia during (a) 2004 and (b) 2004 seasons. Vertical bars indicate standard error of the mean (n = 3).

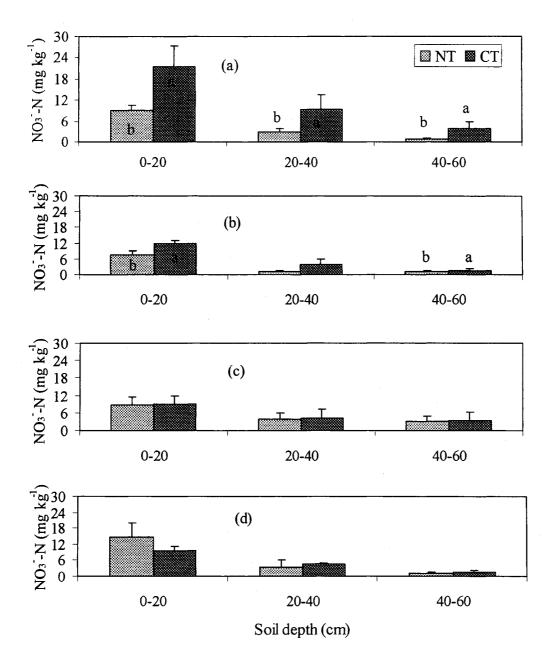


Figure 7.7: Nitrate-N concentrations (mg kg<sup>-1</sup> soil) in the soil profile under no-tillage (NT) and conventional tillage (CT) systems at Streets Ridge (SR) in (a) fall 2003, (b) spring 2004, (c) fall 2004, and (d) spring 2005. Bars within same depth followed by different letters are significantly (p< 0.05) different. Vertical bars are standard error of the mean (n = 3).

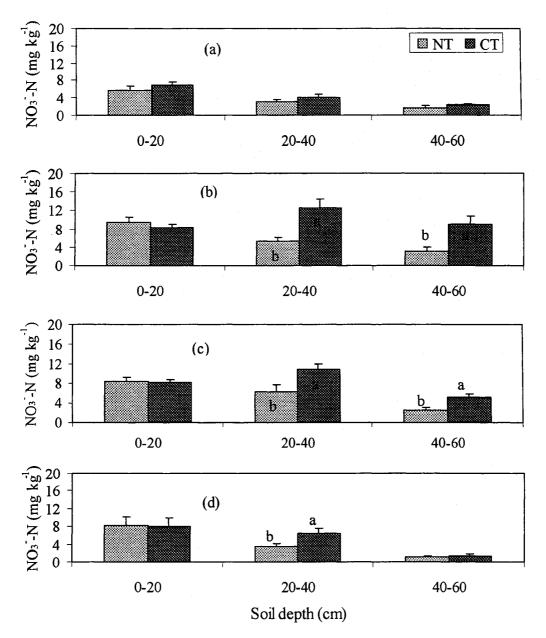


Figure 7.8. Nitrate-N concentrations (mg kg<sup>-1</sup> soil) in the soil profile under no-tillage (NT) and conventional tillage (CT) systems at Bio-Environmental Engineering Center (BEEC) in (a) spring 2004, (b) fall 2004, (c) spring 2005, and (d) fall 2005. Bars within same depth followed by different letters are significantly (p< 0.05) different. Vertical bars are standard error of the mean (n = 5).

# **CHAPTER 8**

Odour Emissions Measurement Using Micro-meteorological Techniques Following

Application of Hog Slurry to Grass

### **ABSTRACT**

Nuisance odours emanating from livestock operations are a major challenge to the nonfarming public. Several field experiments were conducted at Great Village, Nova Scotia to evaluate the effect of management strategies and meteorological conditions on odour emissions from hog slurry applied to grass. Management strategies included slurry application rate, soil water status, slurry dilution with water and rainfall simulation shortly after field application. It was found that doubling (120,000 L ha<sup>-1</sup>) the application rate had no impact on odour emissions. Tripling (180,000 L ha<sup>-1</sup>) the application rate, however, increased emissions, relative to a conventional (60,000 L ha<sup>-1</sup>) application rate. Applying slurry to soil that received water prior to application increased emissions in one of the experiments, compared to soil that did not receive water. On average, diluting slurry with water decreased emissions by only 13%. Meanwhile, rainfall immediately after application increased odour emissions by 15%. Odour fluxes increased with higher windspeed, net radiation and evapotranspiration. Odour emissions can therefore, be reduced by following proper (recommended) application rates, but most importantly, by applying slurry during calm, cool days. However, such stable weather conditions may increase odour persistence due to lack of vertical mixing, reduced transfer rates and slow drying of the slurry.

### **8.1 INTRODUCTION**

Offensive odours emanating from livestock operations are a major nuisance to the non-farming public. The practice of intensive livestock production results in substantial amounts of manure, which in most cases is eventually spread on farm fields. According to Statistics Canada (2001), in 2000, manure was spread over 6.8 million ha, representing an increase of 5.5% over 1995.

Land spreading of manure, in particular, draws more complaints about nuisance odour than any other aspect of livestock production (AAFC, 1998b; Phillips et al., 1991; Williams, 1984). In Quebec, 70% of the complaints surrounding nuisance odour involved land spreading (AAFC, 1998b). In Saskatchewan, Guo et al. (2005) observed that between May and October manure spreading contributed to increased odour occurrences. Odour emissions from field-applied manure are generally affected by management practices and weather conditions. The major weather conditions include atmospheric stability, windspeed, temperature, relative humidity, solar radiation, and the mixing height (Guo et al., 2006). High wind speeds increase odour transfer rate from manure to the air (Smith and Watts, 1994b; Zhou and Zhang, 2003), while a higher temperature stimulates the breakdown of odorous compounds (Le et al., 2005).

Odour is a complex mixture of many different compounds resulting from the anaerobic decomposition of manure (Le et al., 2005; Zhang et al., 2002), and some of these compounds may have negative effects on crops, animals and humans (Hobbs et al., 1999; Le et al., 2005). A significant amount of research has been devoted to quantifying odour emissions from livestock barns and stored manure, with little focus on manure application (Agnew et al.,

2006; Cicek et al., 2004; Jacobson et al., 1999; Zhou and Zhang, 2003). Moreover, the limited studies that measured odour emissions following manure application (Agnew et al., 2006; Chen et al., 2000; Hanna et al., 2000; Lau, et al., 2003; Misselbrook et al., 1993; Rahman et al., 2001; Rahman et al., 2005) have utilised enclosures or wind tunnels, which may provide unrealistic estimates due to their effect on the micro-climate.

Micrometeorological techniques are used to measure the turbulent transfer of gases and fluid particles between the surface and the atmosphere. These techniques typically measure fluxes over extensive areas thus minimising spatial variability (Baldocchi et al., 1988; Pain et al, 1991; Skiba et al, 1996). Among the various micrometeorological techniques, the Theoretical Profile Shape (TPS) method (Wilson et al., 1983) is one of the simplest in relation to physical monitoring. It has been extensively used to study ammonia (NH<sub>3</sub>) flux from field applied manure (Gordon et al. 1988; Gordon et al., 2001; Thompson and Meisinger, 2004; Wilson et al., 1983). With the TPS method, both the gas concentration and windspeed are measured above the centre of the circular plot at a single height referred to as ZINST (Gordon et al., 1988; Pain et al., 1991; Wilson et al., 1983). Although the TPS method has been extensively used for NH<sub>3</sub> volatilisation measurements, its application for quantifying odour emissions following field-spreading of manure has been quite limited (Pain et al., 1991).

The objectives of this study are therefore, to: (i) evaluate the magnitude of odour emissions using the TPS method following the application of hog (Sus scrofa) slurry to Grass, and (ii) identify management and meteorological factors that influence the rate of odour emissions from surface applied slurry. The study specifically compared odour emissions from

different slurry application rates, different initial soil water status, diluted slurry, and rainfall simulation immediately after slurry application.

### 8.2 MATERIALS AND METHODS

## 8.2.1 Experimental Location, Site Description and Design

Several field experiments were conducted during the summers (June to October) of 2003 and 2004 on two acidic soils seeded to forage grass in Great Village, Nova Scotia (45°25′N, 63°36′W). The forage grass was a mixture of timothy (*Phleum pratense*) and meadow fescue (*Festuca pratensis*). In 2003, the soil used was an Acadia (Marshland) fine loam (Gleyed Regosol or Regosol, Canadian and FAO classification). Acadia soils developed on strongly to slightly acid deep level silt loam to silty clay loam, marine sediments and have slow to extremely slow permeability (Webb, et al., 1991; AAFC, 1998a). In 2004, the soil used was a Truro fine sandy loam (Orthic Humo-Ferric Podzol or Orthic Podzol, Canadian and FAO classification). Truro soils developed on fine sandy to coarse loamy glacio-fluvial sediments and are well drained (AAFC, 1998a; Webb, et al., 1991). Physical and chemical characteristics of both soils are shown in Table 8.1.

Experiments were conducted in two of six circular plots, 7 m in diameter and separated by 3 m spacing. To minimise cross contamination, plots were arranged in a straight line perpendicular to the direction of the prevailing wind (Appendix 3). To obtain an even distribution, slurry was applied manually using buckets. Slurry used in all the experiments was collected from a nearby commercial hog operation with characteristics provided in Table 8.1. Before slurry application, the grass was mowed to a height of about 5 cm using a

tractor-drawn mower. Experiment start dates, duration of measurements, treatments, application rates and average meteorological conditions are shown in Table 8.2.

## 8.2.2 Odour Collection, Analysis and Flux Calculations

Immediately following slurry application, odour samples were collected in 10 L Tedlar bags using micrometeorological techniques (Gordon et al., 1988; Pain et al., 1991; Wilson et al., 1983). Odour samples were collected from the centre of each plot at 12.5 cm (ZINST) as discussed by Gordon et al. (1988). Samples were collected using an AC'SCENT vacuum chamber (St Croix Sensory Inc., Stillwater, MN) designed for odour sampling (Appendix 9). During sampling, odour samples are directly drawn into the sample bags without coming into contact with the pump. This reduces chances of sample contamination by gases generated by the pump. The typical time to fill a bag was approximately 10 min. Samples were generally collected at 0, 2, 4, 6, 18, 24, 30 and 48 h after slurry application and sent to AAFC, Charlottetown, Prince Edward Island for subsequent analysis. Due to the high cost of analysing odour samples, only one sample per treatment (no replication) was collected at each sampling time, thus data were not subjected to analysis of variance.

Odour concentrations (OC) were determined using an AC'SCENT dynamic-dilution olfactometer (St Croix Sensory Inc., Stillwater, MN) (Appendix 9) together with an odour panel consisting of six trained panellists. The olfactometer mixes odour samples in specific ratios with odour free air for presentation to the panel. The panellists were each presented with three samples via the olfactometer to test (i.e., sniff) and had to select the sample that contained odorous air. This approach is referred to as the triangular forced choice method

(Zhang et al., 2002). The advantage with olfactometry is that it provides objective data on OC through the determination of threshold values (Pain et al., 1991). An OC is defined as the number of dilutions at which 50% of the panellist can detect an odour, and is expressed as odour units m<sup>-3</sup> (OU m<sup>-3</sup>) of air (Hobbs, et al., 1995; Misselbrook et al., 1997; Steven et al., 2006). Using the theoretical profile shape (TPS) method, odour fluxes (OU m<sup>-2</sup> s<sup>-1</sup>) can be calculated as (Gordon et al., 1988; Pain et al., 1991; Wilson et al., 1983):

$$F = \frac{\overline{SC}}{\left(\frac{\overline{SC}}{F}\right)} \tag{1}$$

where F is the odour flux (OU m<sup>-2</sup> s<sup>-1</sup>),  $\overline{S}$  and  $\overline{C}$  are the windspeed (m s<sup>-1</sup>) and OC (OU m<sup>-3</sup>), respectively, both measured at ZINST (12.5 cm). The ( $\overline{SC}/F$ ) is a dimension-less ratio that has a value of 12 for 7 m diameter plots (Gordon et al., 1988). Total odour emissions for the duration of an experiment are derived by integrating these flux measurements.

Windspeed for flux calculations was recorded at 12.5 cm (ZINST) using an inverted cup anemometer (Met One 014A, Grants Pass, OR). From each plot, soil temperature at 10 cm depth was monitored using copper-constantan thermocouples and soil moisture at the 0-20 cm depth was recorded using time domain reflectometry (TDR). Additionally, several meteorological parameters including net radiation, vapour pressure deficit, relative humidity, soil heat flux and rainfall were measured using a Bowen Ratio Energy Balance (BREB) system (Radiation and Energy Balance System Inc, Seattle, WA) (Appendix 8). Evapotranspiration (ET) rates (mm d<sup>-1</sup>) were calculated using latent heat data computed from

the BREB (Oke, 1996; Peacock and Hess, 2004). Data were recorded at 60 s intervals and averaged over 15 min using a CR10 data-logger (Campbell Scientific Corp., Logan, UT).

#### 8.3 RESULTS AND DISCUSSION

#### **8.3.1 Odour Concentration**

Table 8.3 shows the mean odour OC, the ranges and the percent (%) change in odour emissions measured from each experiment in both 2003 and 2004. The mean OC were low (ranging from 51 to 113 OU m<sup>-3</sup>) compared to other studies, even with the highest application rate. Pain et al. (1991) measured OC ranging from 34 to 1076 OU m<sup>-3</sup> after applying pig or cattle slurry to grass. Rahman et al. (2001, 2005) recorded OC values ranging from 102 to 1053 OU m<sup>-3</sup> after injecting slurry at different rates. Mosley et al. (1998) observed an OC of 250 OU m<sup>-3</sup> soon after surface application of pig slurry, but this declined to about 60 OU m<sup>-3</sup> after 24 h. Misselbrook et al. (1993) reported that typical OC's following pig slurry spreading would be 150 OU m<sup>-3</sup> at source, while Mosley et al. (1998) suggested that OC for background (uncontaminated) air upwind of experiments should range from 50 to 150 OU m<sup>-3</sup>. In the current study, background air samples collected before slurry spreading had OC's ranging from 31 to 99 OU m<sup>-3</sup>. The lower OC's in the current study may be attributed to different soil types, manure characteristics, soil and sward conditions (Rahman et al. 2005), weather conditions, and measurement techniques. Another factor that may have caused the lower OC's may have been due to off-gassing and sorption of odour compounds to Tedlar bags during storage i.e., before analysis (Keener et al., 2002; Trabue et al., 2006). Trabue et al., 2006 found that storing odour samples in Tedlar bags for > 0.5 h resulted in significantly reduced odour concentration, and concluded that odour results from Tedlar bags must be interpreted with caution. In the current study, it was not possible to analyse samples immediately after collection; samples were typically stored for 48 to 72 h before analysis.

### 8.3.2 Odour Fluxes

Odour fluxes were generally high shortly after slurry application and declined with time. There were, however, diurnal fluctuations, due to changes in windspeed and solar radiation. Using the TPS method, Pain et al. (1991) observed similar odour emission patterns after applying cattle and pig slurry. Overall, fluxes ranged from 1 to 30 OU m<sup>-2</sup> s<sup>-1</sup> in 2003, while in 2004, they ranged from 2 to 20 OU m<sup>-2</sup> s<sup>-1</sup>. Agnew et al. (2006) recorded odour fluxes of 40 and 34 OU m<sup>-2</sup> s<sup>-1</sup> for surface and incorporated swine manure, respectively. Using wind tunnels, Rahman et al. (2005) recorded higher odour emission rates (94 to 105 m<sup>-2</sup> s<sup>-1</sup>) after applying liquid swine manure at different rates. In Manitoba, odour emission rates from swine barns ranged from 12 to 38 OU m<sup>-2</sup> s<sup>-1</sup> (Zhou and Zhang, 2003), while in Minnesota they ranged from 1 to 30 OU m<sup>-2</sup> s<sup>-1</sup> (Jacobson et al., 1999). Typical odour emission rates from field-applied pig slurry are summarised by Smith and Watts (1994a), and they range from 3 to 504 OU m<sup>-2</sup> s<sup>-1</sup>.

During all experiments, slurry application rate had no impact on odour fluxes. The only exceptions were the experiments conducted on July 3, 2003 and October 18, 2004, which compared 3x (180,000 L ha<sup>-1</sup>) and 1x (60,000 L ha<sup>-1</sup>) application rates (Figure 8.1).

During these experiments, the 3x rate produced higher odour fluxes, particularly soon after slurry application (Figure 8.1). In 2003, odour fluxes for the 3x rate ranged from 3 to 19 OU m<sup>-2</sup> s<sup>-1</sup>, while those for the 1x rate ranged from 3 to 11 OU m<sup>-2</sup> s<sup>-1</sup>. In 2004, fluxes ranged from 3 to 10 m<sup>-2</sup> s<sup>-1</sup> and 2 to 9 OU m<sup>-2</sup> s<sup>-1</sup> for the 3x and 1x application rates, respectively. After injecting swine slurry at different rates, Rahman et al. (2001, 2005) also found that application rate had no impact on odour emission rates. This suggests that it takes large differences in application rate to detect differences in odour flux using olfactometry.

Soil water content had no effect on odour fluxes. In 2003, at the start of the experiment, volumetric soil water content ( $\theta_v$ ) was 37 and 31% in the plots that received water prior to slurry application and plots that did not receive water, respectively. In 2004, it was 38 and 34% in the plots that received water and plots that did not receive water, respectively. In 2003, odour fluxes in the wetter ( $\theta_v = 37\%$ ) plots were higher than in the dryer ( $\theta_v = 31\%$ ) plots only during the first 4 h after spreading and thereafter remained similar (Figure 8.2). Fluxes in the wetter ( $\theta_v = 37\%$ ) soil ranged from 2 to 22 OU m<sup>-2</sup> s<sup>-1</sup>, while for the other soil ( $\theta_v = 31\%$ ) they ranged from 2 to 14 OU m<sup>-2</sup> s<sup>-1</sup>. In 2004, fluxes in the dryer soil ( $\theta_v = 34\%$ ) were slightly higher than in the wetter soil ( $\theta_v = 38\%$ ), ranging from 2 to 10 OU m<sup>-2</sup> s<sup>-1</sup>, while in the wetter soil they ranged from 3 to 7 OU m<sup>-2</sup> s<sup>-1</sup> (Figure 8.2). These inconclusive results may have been caused by the fact that the  $\theta_v$  for the plots that received water prior to slurry application and plots that did not receive water were not very different, particularly in 2004.

Slurry dilution slightly reduced odour fluxes (Figure 8.3). Fluxes were generally highest soon after slurry application and decreased with time (Figure 8.3). Meanwhile,

rainfall after slurry application slightly increased odour fluxes (data not shown). This may have been caused by the fact that the addition of water reduced the slurry drying process, thus resulting in slightly higher odour fluxes. Watts et al. (1992) reported that odour emission rates from manure increased in the 2 day period following heavy rain and then declined rapidly as the manure dried. Nonetheless, results indicate that slurry dilution and rainfall simulation at the rates used in this study may not be effective in reducing odour fluxes from field-applied hog slurry.

### 8.3.3 Total Odour Emissions

Total odour emissions (OU m<sup>-2</sup>) and the percent (%) change in odour emissions for all experiments are shown in Table 8.4. These results show that in general, increasing slurry application rate resulted in greater odour emissions, particularly when the application rate increased to 3x. At this application rate, total odour emissions were on average 26% (range 11 to 42%) higher than the conventional (1x) rate. Similar to odour flux, applying slurry on soils that had received water produced variable results. In the experiment conducted on July 22, 2003, total emissions increased by 4% when slurry was applied on soil that had received water, while in the experiment conducted on July 28, 2004, emissions decreased by 18%. Such contrasting results were unexpected, and may have been caused by the fact that the  $\theta_v$  for the plots that received water and those that did not receive water were not very different. Diluting slurry decreased emissions on average by only 13% (range 4 to 26%). In a laboratory experiment, Le et al. (2005) found that increasing manure dilution from 0 to 100%

decreased odour emissions by 50%. Meanwhile, rainfall after slurry application increased emissions by 15%. These results suggest that both slurry dilution and rainfall after application at the rates used in this study may not be viable strategies for reducing odour emissions from field-applied pig slurry. These results should however, be interpreted with caution knowing that treatments were not replicated, thus the data were not subjected to analysis of variance.

## 8.3.4 Impact of Meteorological Variables on Odour Emissions

To establish possible relationships between meteorological variables and odour emissions, the average odour fluxes (OU m<sup>-2</sup> s<sup>-1</sup>) for all conventional (1x) treatments in the 24 h following slurry application were used in the linear regression analysis. Out of the ten meteorological variables tested, only three were correlated with odour flux during both years (Figure 8.4). Fluxes increased with higher windspeed, net radiation and evapotranspiration. In 2003, the strongest correlation was with windspeed ( $R^2 = 0.98$ ), while in 2004, it was with evapotranspiration ( $R^2 = 0.97$ ). Using wind tunnels, Smith and Watts (1994b) and Schmidt et al. (1999) observed that odour emission rates from manure increased with windspeed. Meanwhile, Smith and Watts (1994b) suggested that evaporation of water from dying soil provides a guide to the likely process of odour emission. In 2004, the relationship with evapotranspiration was, however, weak yielding an  $R^2$  of only 0.27.

Both air and soil temperature poorly correlated with odour flux. In a laboratory experiment, Le et al. (2005) found that raising temperature from 10 to 30°C increased odour emission by 216%. When studying odour emissions from swine barns, Zhou and Zhang

(2003) reported that odour emission rates were not affected by outdoor air temperature in the range from 12 to 35°C. In the current study, average air temperature during odour measurements was 19°C in 2003 and 16°C in 2004 (Table 8.2). Nonetheless, results suggest that odour emissions can be reduced by applying slurry when windspeed, net radiation and evapotranspiration rates are low. Incidentally, this will also reduce NH<sub>3</sub> volatilisation. This may, however, lead to increased odour persistence since there will be less dilution of odour (i.e. less vertical mixing) and transfer rates and slow drying of the slurry.

## **8.4 CONCLUSIONS**

Odour fluxes were generally highest soon after slurry spreading and decreased with time. Compared to the conventional application rate, doubling the slurry application rate had no effect on odour fluxes, but tripling the application rate increased odour fluxes and subsequently odour emissions. Applying slurry to wet soil produced somewhat variable results. Meanwhile, diluting slurry decreased odour emissions by an average 13%, while rainfall simulation increased emissions by 15%. Odour fluxes increased with higher windspeed, net radiation and evapotranspiration. Thus, slurry spreading should be done during less windy, cool days (low evaporative demand) in order to reduce odour emissions, however, such weather conditions may increase odour persistence. Due to lack of replication, these results should be interpreted with caution.

**Table 8.1.** Chemical and physical characteristics of the soils (0-20 cm depth) and hog slurry used in the study.

Characteristic	Acadia Soil 2003	Truro Soil 2004	Slurry 2003	Slurry 2004
pН	4.71#	6.05#	6.22	5.81
TN (%)	0.33	nd	0.36	0.28
C (%)	3.80	nd	1.41	1.06
C:N ratio	11.5	nd	3.92	3.79
NH <sub>4</sub> +-N (%)	nd	nd	0.24	0.20
NO <sub>3</sub> -N (mg kg <sup>-1</sup> )	2.2	14.3	nd	nd
Dry matter (%)	na	na	3.96	2.49
Porosity (%)	58.5	49.4		
Bulk Density (Mg m <sup>-3</sup> )	1.10	1.34		
Organic Matter (%)	6.50	5.05		
CEC (meq/100g)	14.1	11.3		

nd = not determined, na = not applicable, \*pH 1:2 dry soil: de-ionised water, TN and C determined using CNS analyser.

<sup>&</sup>lt;sup>¶</sup>Taken from Webb et al., 1991.

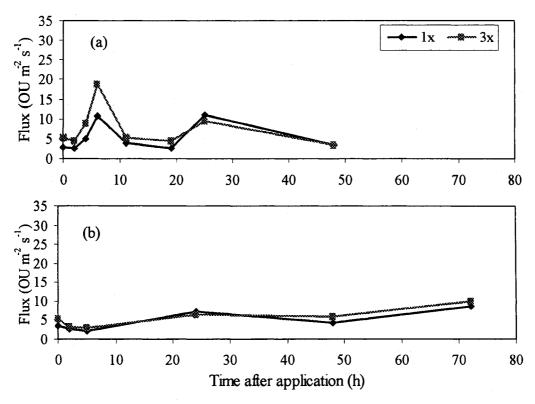
conditions i.e. air temperature (air temp), windspeed, net radiation, vapour pressure deficit (VPD) and relative humidity (RH) in Table 8.2. Summary of experiments, start dates, duration of measurement, treatments compared and average meteorological 2003 and 2004.

Type of	Experiment	Duration of	Treatments	Av	erage Me	Average Meteorological Conditions	l Condit	ions
nami jadya	Staff date	Measurement (h)		Air Temp (°C)	Wind- speed (m s <sup>-1</sup> )	Net Radiation $(W m^{-2})$	VPD kPa	RH %
Application	6 <sup>th</sup> Jun 2003	42	60,000 vs. 120,000 L ha <sup>-1</sup>	13.9	1.06	200	0.24	89.4
Rate	20th Jun 2003	42	60,000 vs. 120,000 L ha <sup>-1</sup>	20.9	0.87	231	0.79	9.07
	3 <sup>rd</sup> July 2003	48	60,000 vs. 180,000 L ha <sup>-1</sup>	21.7	0.88	173	0.51	82.5
	12th Sep 2003	48	60,000 vs. 120,000 L ha <sup>-1</sup>	18.9	1.79	312	1.01	0.99
	7 <sup>th</sup> Jun 2004	7.1	60,000 vs. 120,000 L ha <sup>-1</sup>	17.2	0.97	259	0.85	74.6
	18th Oct 2004	72	60,000 vs. 180,000 L ha <sup>-1</sup>	13.7	0.92	199	0.75	74.8
Soil Water	22 <sup>nd</sup> Jul 2003	42	86 mm (wet) vs. No water	22.3	1.27	189	0.52	87.1
Status	28 <sup>th</sup> Jul 2004	42	31 mm (wet) vs. No water	21.0	0.68	285	0.64	83.4
Slurry	25th Aug 2003	48	25% water (volume)	17.5	1.56	268	1.14	61.5
Dilution	18 <sup>th</sup> Jun 2004	72	50% water (volume)	17.2	1.26	1	ł	;
	21st Sep 2004	72	100 % water (volume)	12.2	1.26	315	08.0	63.2
Rainfall	21st Sep 2004	72	6 mm water	12.2	1.26	315	8.0	63.2
Simulation								

Table 8.3. Odour concentration (OC) range, mean OC (OU m<sup>-3</sup>), total odour emission and % change for different experiments in 2003 and 2004.

Experiment start date	Treatments <sup>¶</sup>	OC	Mean	Total odour	% change
	·	Range (OU m <sup>-3</sup> )	OC (OU m <sup>-3</sup> )	emissions ×10 <sup>6</sup> (OU m <sup>-2</sup> )	in emissions
2x	1-180	101	1.14	•	
20 <sup>th</sup> Jun 2003	1x	50-100	80	0.81	1
	2x	63-142	86	0.82	
3 <sup>rd</sup> Jul 2003	1x	33-89	66	0.91	42
	3x	58-156	97	1.29	
12 <sup>th</sup> Sep 2003	1x	99-126	113	2.80	-11
	2x	62-126	104	2.49	
7 <sup>th</sup> Jun 2004	1x	25-79	46	0.91	8
	2x	25-89	51	0.98	
18 <sup>th</sup> Oct 2004	1x	50-89	65	1.46	11
	3x	67-135	80	1.62	
22 <sup>nd</sup> Jul 2004	No water	40-89	65	0.85	4
	Water	35-135	69	0.88	
28 <sup>th</sup> Jul 2004	No water	44-203	101	1.20	-18
	Water	55-114	78	0.99	
25 <sup>th</sup> Aug 2003	Undiluted	44-126	82	1.13	-4
	Diluted (25%)	40-113	79	1.08	
18 <sup>th</sup> Jun 2004	Undiluted	56-142	83	1.99	-26
	Diluted (50%)	39-112	64	1.47	
21st Sep 2004	Undiluted	50-112	68	1.21	-9
	Diluted (100%)	38-112	66	1.10	<del> </del>
21st Sep 2004	No Rainfall	50-118	68	1.21	15
	Rainfall (6 mm)	37-118	77	1.39	

 $<sup>^{\</sup>P}1x$ , 2x and 3x represent 60,000, 120,000 and 180,000 L ha<sup>-1</sup>, respectively



**Figure 8.1.** Effect of slurry application rate on odour flux (OU m<sup>-2</sup> s<sup>-1</sup>) in (a) 2003 and (b) 2004. Application rates used were conventional (1x) and triple (3x).

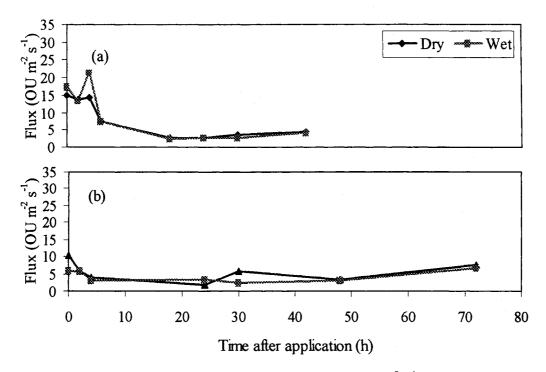


Figure 8.2. Effect of soil water status on odour flux (OU m<sup>-2</sup> s<sup>-1</sup>) following surface application of hog slurry to grass in (a) 2003 and (b) 2004.

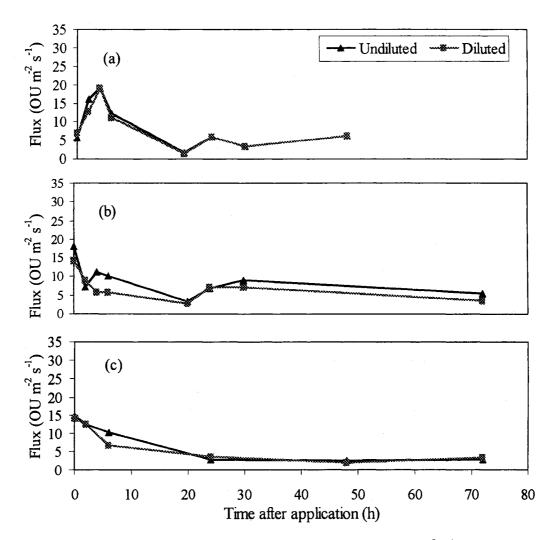


Figure 8.3. Effect of hog slurry dilution on odour flux (OU  $m^{-2}$  s<sup>-1</sup>) for (a) 25% dilution, (b) 50% dilution, and (c) 100% dilution (v/v).

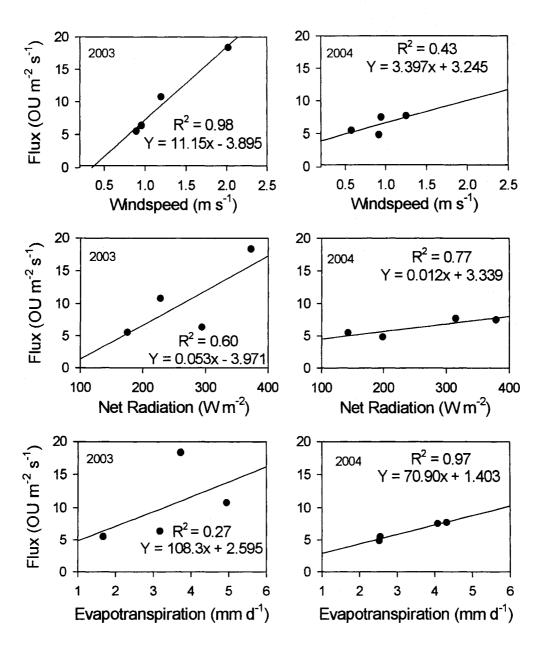


Figure 8.4. Relationship between odour flux (OU m<sup>-2</sup> s<sup>-1</sup>) and meteorological variables (windspeed, net radiation, and evapotranspiration) following application of hog slurry to grass in 2003 and 2004.

## CHAPTER 9

## 9.1 CONCLUSIONS AND RECOMMENDATIONS

From the laboratory and field studies which evaluated the impact of management practices and meteorological conditions on  $NH_3$ ,  $N_2O$  and odour emissions after hog slurry application, the following overall conclusions can be drawn:

- (1) Dicyandiamide had no effect on N<sub>2</sub>O emissions and therefore mixing it with hog slurry will probably not be a viable strategy to mitigate emissions from these acidic soils.
- (2) Liming soil lowered N<sub>2</sub>O emissions and simultaneously increased NH<sub>3</sub> volatilisation, thus resulting in a partial tradeoff between the two gases. Nonetheless, emissions of both gases can be limited by liming soil to a pH of approximately 6.3; incidentally, most agricultural crops grow well at this soil pH.
- (3) Slurry application rate had no impact on N<sub>2</sub>O emissions. Conversely, NH<sub>3</sub> volatilisation and to a lesser extent odour emissions increased with application rate. Hence, following proper (recommended) application rates will reduce environmental pollution associated with slurry spreading.
- (4) Applying slurry to wet soils had no impact on N<sub>2</sub>O and odour emissions, but increased NH<sub>3</sub> emissions, therefore, this practice should be avoided.
- (5) Slurry dilution decreased  $NH_3$  losses and to a lesser extent odour emissions, but had no effect on  $N_2O$  emissions. In the mean time, a 6 mm rainfall after slurry application reduced  $NH_3$  losses without increasing  $N_2O$  emissions, but slightly increased odour emissions.
- (6) Nitrous oxide losses from potassium nitrate fertiliser were higher than those from hog slurry and ammonium sulphate fertiliser, indicating that NO<sub>3</sub>-N availability is the main

controller of  $N_2O$  production in these acidic soils. Hence,  $N_2O$  emissions can be minimised by applying  $NH_4^+$  based fertilisers including hog slurry, rather than  $NO_3^-$  based fertilisers.

- (7) Ammonia volatilisation increased with air and soil temperature, net radiation, evapotranspiration rates, and vapour pressure deficit, while N<sub>2</sub>O emissions were not affected by the recorded meteorological conditions. Meanwhile, odour emissions increased with higher windspeed, net radiation and evapotranspiration rates. Consequently, NH<sub>3</sub> and odour emissions can be somewhat reduced by applying slurry during cool and calm conditions.
- (8) Considering the fact that estimated indirect N<sub>2</sub>O emissions (i.e., emissions due to volatilised NH<sub>3</sub>) were generally higher than direct (measured) emissions, more emphasis should be directed towards reducing NH<sub>3</sub> losses in these acidic soils.

From the study that evaluated the impact of tillage system on gaseous N and NO<sub>3</sub>-N losses after cattle manure application, the following overall conclusions were drawn:

(9) Ammonia losses,  $N_2O$  and denitrification rates were higher under NT than CT. However,  $N_2O:N_2O+N_2$  ratios were lower in NT, suggesting more complete reduction of  $N_2O$  to  $N_2$  under NT. In addition,  $NO_3$ -N concentrations in the soil profile and tile drainage water were lower in NT, partly due to enhanced denitrification. Thus, NT can be used to reduce  $NO_3$ -N leaching to groundwater, although with tradeoffs.

## 9.2 CONTRIBUTIONS TO THE ADVANCEMENT OF KNOWLEDGE

There is increasing concern surrounding N losses from manure. Such losses arise through emissions to the atmosphere and leaching to groundwater. Additionally, manure spreading activities often cause complaints about their associated nuisance odours. Therefore, identifying management practices that conserve manure N and reduce environmental pollution associated with manure is paramount. This study provides new insights on NH<sub>3</sub>, N<sub>2</sub>O, denitrification, N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratios and NO<sub>3</sub>-N leaching and odour emissions following application of manure to grassland and cultivated systems under Nova Scotia acid soils and climatic conditions.

(i) The study evaluated the impact of adaptive management practices and meteorological conditions on NH<sub>3</sub>, N<sub>2</sub>O and odour emissions following application of liquid hog manure to acid grassland soils. While the effects of manure application on NH<sub>3</sub> and N<sub>2</sub>O have been extensively investigated elsewhere, these studies were conducted separately and did not include odour emissions. Several studies have raised the concern that management strategies adopted to reduce emissions of one gas may lead to an increase in the other gas, thus offsetting any gains. This study is therefore unique in that it looked at NH<sub>3</sub>, N<sub>2</sub>O and odour emissions simultaneously.

It was found that  $N_2O$  emissions from hog slurry applied to acid soils are low even with high application rates, due to slow nitrification activity. The study also found that  $N_2O$  production in acidic soils is controlled by  $NO_3^-$  availability and that  $N_2O$  emissions can be minimised by applying  $NH_4^+$  based fertilisers including hog slurry rather than  $NO_3^-$  based

fertilisers. In addition, estimated indirect N<sub>2</sub>O emissions (i.e. emissions due to volatilised NH<sub>3</sub>) were higher than direct (measured) emissions, indicating that more emphasis should be directed towards reducing NH<sub>3</sub> losses from these acidic soils. Soil and environmental conditions play a major role in NH<sub>3</sub> and N<sub>2</sub>O emissions and therefore have to be considered when spreading manure.

(ii) With regard to odour, a significant amount of research has been dedicated to quantifying odour emissions from barns and stored manure. However, little has been done following field application of manure, yet most complaints about nuisance odour occur during spreading. Moreover, the majority of studies that looked at odour after manure spreading used wind tunnels for odour measurement, which tend to alter the micro-climate over the covered surface. This study used micrometeorological techniques. To the best of my knowledge, there is only one published study, which examined odour emissions from field-applied manure using micrometeorological techniques. Findings the current study will contribute towards building a scientific basis for better understanding of management practices and meteorological conditions that impact odour emissions.

The study showed that odour emissions from field-applied hog slurry were low. Treatment differences could not be detected mainly due to high variability of odour concentrations associated with both sampling and olfactometry procedures. Odour emissions were enhanced by higher wind speed, net radiation and evapotranspiration, suggesting that emissions can be reduced by applying slurry during cool, calm days.

(iii) While effects of tillage systems on denitrification rates and  $N_2O$  emissions have been extensively investigated elsewhere, few field studies have been published on the variations in the  $N_2O:N_2O+N_2$  ratio under different tillage systems following manure application. Most such studies have been conducted in the laboratory using inorganic fertiliser and it is doubtful if these results can be extrapolated to field conditions. This study evaluated the impact of tillage system on  $NH_3$ ,  $N_2O$ , denitrification,  $N_2O:N_2O+N_2$  ratios and  $NO_3$  leaching following field-application of manure. To the best of my knowledge, this represents the first time all these N loss forms have been studied simultaneously following manure application.

The study showed that NH<sub>3</sub> losses, denitrification rates and N<sub>2</sub>O emissions in NT were higher than in CT. Nevertheless, N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratios were lower in NT, indicating more complete reduction of N<sub>2</sub>O to N<sub>2</sub> in NT. Likewise, soil and drainage water NO<sub>3</sub>-N concentrations were lower in NT, partly due to higher denitrification. Therefore, NT can be used to reduce NO<sub>3</sub>-N leaching to groundwater, although with trade-offs.

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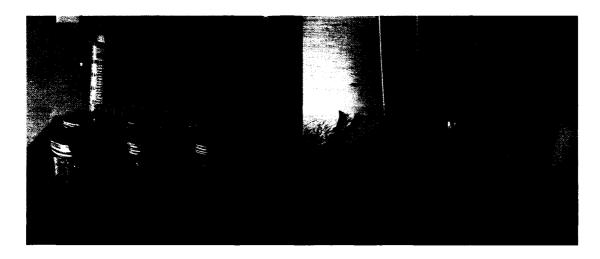
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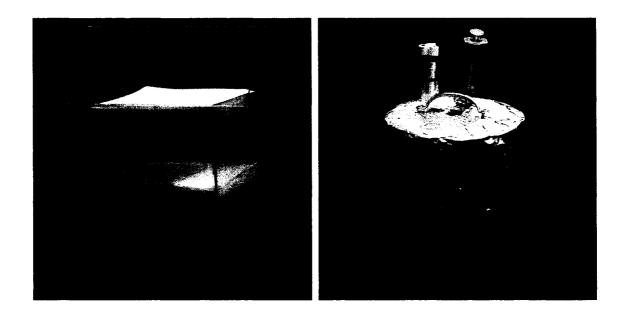
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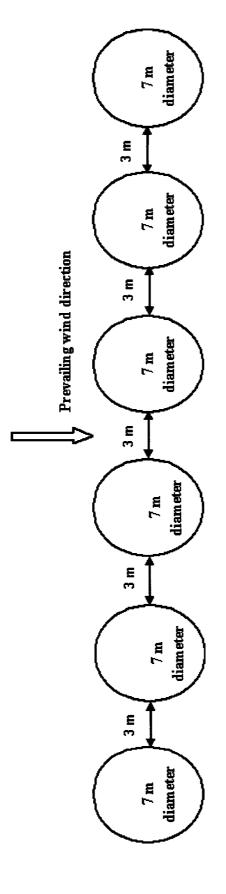
# **APPENDICES**



Appendix 1. Mason jars with syringe and titration apparatus used for  $NH_3$  and  $N_2O$  emissions measurements during laboratory experiments.



**Appendix 2.** (a) Static chamber (trap) and (b) vented static chamber used for ammonia (NH<sub>3</sub>) and nitrous oxide (N<sub>2</sub>O) emissions measurements, respectively, during field experiments.



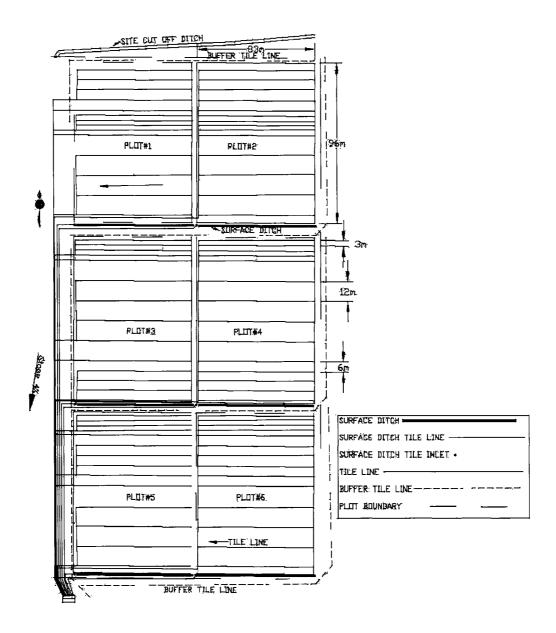
m. Plots were used for assessment of ammonia (NH<sub>3</sub>), nitrous oxide (N<sub>2</sub>O) and odour emissions. Odour samples were collected Appendix 3. Plot layout at Great Village, Nova Scotia in 2003 and 2004. Plots measured 7 m diameter and were separated by 3 from the centre of two plots having different treatments at 12.5 cm (Gordon et al., 1988).



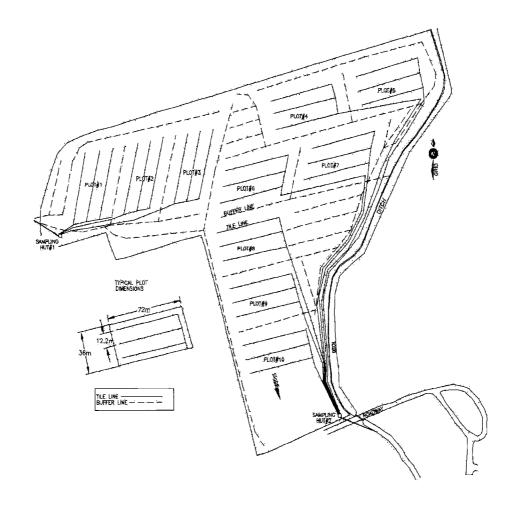
**Appendix 4.** Wind tunnels used for ammonia (NH<sub>3</sub>) flux measurements at Great Village, Nova Scotia in 2005. To prevent cross contamination, plots were arranged in a straight line perpendicular to the direction of prevailing wind (shown by arrow).



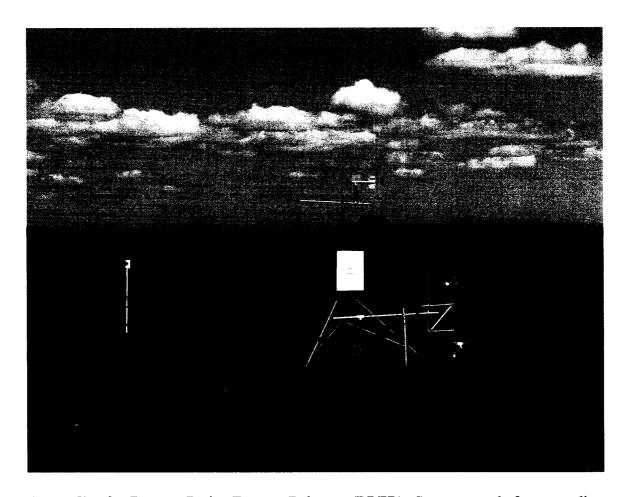
**Appendix 5.** Plot layout with vented static chambers used for nitrous oxide ( $N_2O$  flux measurements at Great Village, Nova Scotia in 2005. Each plot measured 1 m x 1 m separated by 1 m.



**Appendix 6.** Plot layout with drainage and treatment details at Streets Ridge (SR), Nova Scotia. Plots 1, 3 and 6 were no tillage (NT) while plots 2, 4 and 5 were conventional tillage (CT).



**Appendix 7.** Plot layout with drainage and treatment details at Bio-Environmental Engineering Centre (BEEC), Truro, Nova Scotia. Plots 1, 4, 6, 7 and 10 were no tillage (NT) while plots 2, 3, 5, 8 and 9 were conventional tillage (CT).



**Appendix 8:** Bowen Ratio Energy Balance (BREB) System used for recording meteorological data which were subsequently used for calculating evapotranspiration (ET) rates.



**Appendix 9.** (a) Vacuum chamber used for collecting odour samples (insert inflated odour bag) and (b) Olfactometer used for analysing odour concentration.