# Measurement and Simulation of Nitrous Oxide Fluxes from Perennial Forage Grasses and Annual Crops Amended with Pig Manure and Inorganic Fertilizer

by

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## ABSTRACT

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Crop and nutrient management on agricultural soils are essential considerations for mitigating greenhouse gas emissions in our environment. This thesis aimed to simulate and compare nitrous oxide ($N_2O$) fluxes from perennial forage grasses (FPP) and annual crops (ANN) amended with solid pig manure (SPM), liquid pig manure (LPM) and inorganic urea fertilizer (FER). Two field studies were carried out at different sites Carman and Carberry, Manitoba, Canada. At Carman, $N_2O$ fluxes were monitored from FPP following its termination and restoration. At the Carberry, $N_2O$ fluxes were measured from LPM applied to soil annually at a rate of 56,000 L ha$^{-1}$, FER applied at the equivalent rate as total available N from the LPM and un-amended control (CON) plots. At Carberry, in 2011 and 2014 when applied manure N was low, emission factor and emission intensity from LPM was one-half of that from FER. At Carman, the result showed that the termination of perennial forage grasses in combination with applied manure leads to increased soil nitrogen content and $N_2O$ fluxes. However, when FPP were replanted in 2014, $N_2O$ emission from FPP was 30% less than that from ANN treatments. The data from the Carman site were used to evaluate the performance of the DeNitrification-DeComposition (DNDC) model to predict soil moisture and $N_2O$ fluxes. The DNDC model output compared well with the field observed values on the ANN (cumulative $N_2O$ flux and daily soil moisture Nash–Sutcliffe efficiency (NSE) > 0.7) but not on the FPP (cumulative $N_2O$ flux and daily soil moisture NSE < 0.2). In spite of the wide use of the DNDC model, some routines in the model still needs work as seen on the FPP. In

conclusion, perennial forage grass planted in rotation with annual crops can provide N saving benefits, but the N would be lost when the forage grasses are converted to annual cropland. Also, LPM can provide nutrient to crop more efficiently than FER, as less $N_2O$ was emitted to produce a unit grain of wheat, but the nutrient would be lost when applied beyond crop need. Consequently, adequate consideration for mineralizable residue from plowed down forage grasses and applied manure N may help prevent future losses.

# FOREWORD

This thesis has been prepared in the manuscript format following the thesis guidelines of the Department of Soil Science and Faculty of Graduate Study.

Chapter 2 has been published in the Canadian Journal of Soil Science and the corrections from the reviewers have been incorporated into this thesis with some minor changes in presentation and wording based on committee suggestions.

**Adelekun, M**., Akinremi, O., Tenuta, M., Nikièma, P., 2019. Soil nitrous oxide emissions associated with the conversion of forage grass to annual crop receiving an annual application of pig manure. Can. J. Soil Sci. 99: 420–433.

Chapter 3 has been submitted for publication in Agriculture, Ecosystems & Environment (AGEE) journal and is currently under review

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Chapter 4 will be submitted for publication shortly.

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For all the chapters in this thesis, Mayowa Adelekun collected the field data, performed laboratory and data analysis, carried out model calibration and validation, managed literature searches and wrote the first draft of the manuscripts (80 % contribution)

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## NOMENCLATURE AND ACRONYM

| | |
|---|---|
| ANN | Annual crop |
| $b$ | Empirical soil parameter |
| $C$ | Model calculated values |
| $\bar{C}$ | Mean of calculated data |
| $CH_4$ | Methane |
| $CO_2$ | Carbon dioxide |
| CON | Control unamended |
| $C_i$ | Model calculated value of ith iteration |
| EF | Emission factor |
| EI | Emission intensity |
| FC | Field capacity |
| FER | Urea fertilizer |
| FPP | Perennial forage grasses |
| GHG | Greenhouse gas |
| $H_2O$ | Water |
| $i$ | iteration count |
| LPM | Liquid pig manure |
| $k$ | Relative conductivity |
| $K_h$ | Unsaturated hydraulic conductivity (L $T^{-1}$) |
| $K_s$ | Saturated hydraulic conductivity (L $T^{-1}$) |
| *m1* | Clapp and Hornberger emperical parameter |
| *m2* | Clapp and Hornberger emperical parameter |
| MASL | Meters above sea level |
| *ME* | Mean error |
| $n$ | Number of observations |
| N | Nitrogen |
| $N_2$ | Nitrogen gas |
| $N_2O$ | Nitrous oxide |
| $NH_4^+$ | Ammonium ion |
| $NO_3^-$ | Nitrate ion |
| NRMSE | Normalized root mean square error |
| *NSE* | Nash-Sutcliffe Efficiency |
| $O$ | Field observed values |
| $\bar{O}$ | Mean of observed data |
| $O_i$ | Field observed value of ith iteration |

| | |
|---|---|
| PWP | Permanent wilting point |
| $R^2$ | Coefficient of determination |
| *RMSE* | Root Mean Square Error |
| SPM | Solid pig manure |
| $W$ | Volumetric water content or soil wetness ($L^3$ $L^{-3}$) |
| WFPS | Water filled pore space |
| $W_i$ | Water content where retention curve has inflection = 0.92 ($L^3$ $L^{-3}$) |
| $\theta$ | Volumetric water content ($L^3$ $L^{-3}$); |
| $\theta_h$ | Volumetric water content ($L^3$ $L^{-3}$); |
| $\theta_r$ | Residual water content ($L^3$ $L^{-3}$) |
| $\theta_s$ | Water content at saturation ($L^3$ $L^{-3}$) |
| $\Sigma$ | Summation |
| $\psi$ | Matric suction (L) |
| $\psi_i$ | Matric suction at inflection point (L) |

# 1. INTRODUCTION

## 1.1 Background information

Anthropogenically increased concentration of greenhouse gases (GHG) is a known cause of global warming. According to the Intergovernmental Panel on Climate Change (IPCC 2014), the agricultural sector accounts for 14% of global greenhouse gas production in 2010. The three common GHG emitted from the agricultural sector are $CO_2$, $N_2O$ and $CH_4$. Of the 699 Mt $CO_2$ eq of GHG from Canada in 2012, $N_2O$ accounted for 48 Mt $CO_2$ eq (7 %) (Environment Canada 2014). Nitrous oxide is the most powerful greenhouse gas, also capable of degrading the stratospheric ozone layer (Ravishankara et al. 2009). Annually 2.9 Gt of $N_2O$ is emitted from agriculture (IPCC 2014).

The global human population is projected to exceed nine billion in 2050 (FAO 2009). Agriculture is the only viable option of feeding the ever-growing population. When crops are grown, they need nutrients supplied by the soil and this nutrient supply needs to be in balance to avoid soil mining. Nutrient addition through manure, fertilizer or cover crops is needed regardless of growing crop. However, when nutrients are added in excess of plant demand, they may be lost to the environment, causing environmental pollution. Examples of the negative impact of excess nutrients include surface and groundwater pollution and the emission of greenhouse gases (Singh et al. 2019; Thangarajan et al. 2013). When fertilizer or manure is added to soil, it undergoes a series of processes before the release of nutrients needed by the plant. Some of these processes include decomposition, fermentation, mineralization, nitrification and denitrification. Nitrous oxide ($N_2O$) is produced in the soil during the processes of nitrification and denitrification.

There is a need to understand the daily and seasonal variations of the GHG gases from various agricultural management practices in order to mitigate its emission. Continuous monitoring of the GHGs will help gather data that can be used to estimate the emission of these gases. These flux measurements can be used to test and calibrate simulation models that can be used to estimate fluxes beyond the experimental field. This thesis measured and simulated nitrous oxide fluxes from agricultural soils with difference crop and nutrient management practices.

## 1.2 Processes that affect nitrogen cycling and greenhouse gas flux in soil system

### 1.2.1 Decomposition and Fermentation

Decomposition is a process of breaking down complex substances to simple ones. When organic material is added to the soil, it undergoes a process of decay whereby the material is transformed into simpler materials and inorganic substances (Ajwa and Tabatabai 1994). This process is both physical and biochemically mediated (Lehmann and Kleber 2015). Just as in respiration, $CO_2$, and $H_2O$ are typical by-products of decomposition accompanied by the release of plant nutrients and energy. Decomposition is a redox reaction that is catalysed by microbial enzymes. The decomposition of organic materials like manure are controlled by various factors such as temperature, moisture, the composition of the material and the decaying microorganism itself such as bacterial and fungi (Ige et al. 2015). In the process, mineral elements from decomposing organic material are released into the soil for plant use, while gaseous compounds such as $N_2O$ and $CO_2$ are released into the atmosphere. To obtain energy, microorganisms that decompose organic materials respire, releasing $CO_2$ into the atmosphere. Depending on the nature of the decomposing material, prevailing environmental conditions and decay organisms, decomposition may take a short to a long time to complete (Schmidt et al. 2011). The rate of decomposition of organic materials usually follows a simple first-order kinetic (Coleman et al. 2004).

In the absence of oxygen, inorganic and organic substances are used as a terminal electron acceptor in the process of anaerobic respiration. Using organic materials as an electron acceptor, releases acid, alcohol, or gaseous compounds. Organic materials are converted to acetic acid, releasing hydrogen gas. The acetic acid thus formed, is finally converted to methane gas and $CO_2$. This reaction is catalysed by methanogens of which Archea are the major organisms responsible for methanogenesis.

### 1.2.2 Nitrification

The sequential conversion of ammonium-N to nitrite and then to nitrate is referred to as nitrification. It is a two-stage process as described in equations 1 and 2 bellow (Norton and Stark 2011). In the first process, ammonia oxidising bacteria, *Nitrosomonas spp* and *Nitrosopira spp* transforms ammonium to nitrite with the aid of enzyme ammonia monooxygenase (responsible for converting ammonia to hydroxylamine) and Hydroxylamine oxidoreductase (responsible for conversion of hydroxylamine to nitrite). *Nitrobacter* and *Nitrospira* are nitrite oxidising bacteria that transform nitrite to nitrate in the second stage (Del Grosso et al. 2008; Sahrawat 2008). Ammonium from nitrogen fertilizers and pig manure are good substrates for the nitrification process.

$$NH_3 + O_2 + 2H^+ + 2e^- \longrightarrow NH_2OH + H_2O \longrightarrow NO_2^- + 5H^+ + 4e^- \quad [1]$$

$$NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^- \quad [2]$$

Nitrate and nitrous oxide are important products from nitrification that are of environmental concern. Nitrous oxide can easily be lost to the atmosphere by gaseous exchange and it has been reported to be a potent gas capable of global warming and ozone layer depletion (Neubauer and

Megonigal 2015). In like manner, nitrate can easily be leached to groundwater and has been reported to cause methemoglobinemia a baby syndrome that affects skin coloration (Parvizishad et al. 2017).

### 1.2.3 Denitrification

Another process by which a greenhouse gas is released from the soil is through denitrification. In the absence of oxygen, nitrate or nitrite is used as an electron acceptor during microorganism respiration. It is a stepwise reduction of nitrate or nitrite to dinitrogen gas with the release of other intermediates in the process such as NO and $N_2O$ (Equ. 3) (Groffman et al. 2006; Philippot et al. 2007). Denitrification is an essential process in the nitrogen cycle carried out by facultative anaerobes. It is also an energy-yielding process (Hofstra and Bouwman 2005; Saggar et al. 2013).

$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2 \qquad [3]$$

$$2NO_3^- + 10e^- + 12H^+ \longrightarrow N_2 + 6H_2O \qquad [4]$$

Just as in the nitrification process, $N_2O$ may also be lost to the atmosphere during the denitrification process, which makes the process an environmental concern. On the other hand, denitrification may serve as a sink for nitrate in the soil; this is of importance because the process breakdown nitrate formed during the nitrification process thus reducing nitrate loading in groundwater system (Iqbal et al. 2015).

### 1.2.4 Nitrifier-denitrification

Kool et al. (2011) and Wrage et al. (2001) reported that a wide range of processes could produce $N_2O$ fluxes in the soil, which can be attributed to nitrification and denitrification. They indicated that some nitrifiers are also capable of denitrifying which they called the special attributes of ammonia-oxidizing bacteria. They explained that the first stage in nitrifier-denitrification is attributed to nitrification, a process in which ammonia is oxidized to nitrite and then nitrate, while the second stage which is reduction of nitrite and nitrate is attributed to denitrification. As such, they have called for the need to differentiate nitrifier-denitrification from sole nitrification or denitrification process because it also contributes reasonable amounts of $N_2O$ to the environment.

## 1.3 Factors influencing decomposition, nitrification, denitrification and nitrous oxide production in agricultural soils

The basic factors controlling decomposition, nitrification, denitrification and greenhouse gas production in soil can be categorised into proximal and distal scales (Firestone and Davidson 1989). The cellular factors that regulate carbon and nitrogen dynamics (oxygen, nitrate and organic carbon) on a proximal scale are regulated by the environmental and climatic factors such as precipitation and temperature on a distal scale (Zhang et al. 2015). The microbial communities are key players in the greenhouse gas release process. They are mostly affected by primary substrates needed for their biomass building, which include oxygen, nitrogen, and carbon in the soil (Barton et al. 1999).

### 1.3.1 Temperature

Temperature has a significant effect on all living organisms. Temperature on a distal scale is influenced by the climatic and weather conditions of an area. Air temperature fluctuates daily and seasonally, which in turns affects soil temperature. Temperature affects microbial respiration rates (Cho et al. 1997). Like many biochemical reactions, decomposition, nitrification and denitrification rate fluctuates exponentially with temperature changes. The diurnal variation of GHG flux follows a similar pattern to the diurnal variation of soil temperature (Smith et al. 1998).

This reflects the changes in the activity of nitrifiers, denitrifiers and decomposers in the soil system in response to changes in soil temperature. The majority of these organisms are mesophilic; the optimum temperature that is favourable for their growth and reproduction ranges from 25 °C to 37 °C. In contrast their activity declines at a temperature above 45 °C (Coyne 2008). Soil temperature affects the rate of organic matter decomposition in soil, which makes carbon and nitrogen substrates available for organisms in the soil (Hofstra and Bouwman 2005). Temperature also affects the rate of evapotranspiration in the soil-plant system, which in turn affects the moisture content. Soil moisture, vegetal-cover and soil albedo are important factors that affect the soil temperature in return.

### 1.3.2 Moisture

Moisture content affects nitrification and denitrification processes in soil both on proximal and distal scales. The cells of microorganisms are made up of water, too dry a condition may lead to the death of cells if they are not protected. Soil moisture content affects the oxygen concentrations in the pore spaces of the soil. Moisture content also affects the rate at which microorganisms can decompose organic materials in the soil, which in turn makes available the nitrogen and carbon needed for the nitrification and denitrification processes. When fertilizers are added to soil, water is required to dissolve it. Urea, for example, needs water to be hydrolysed to ammonium which in turn is nitrified to nitrate that serves as a primary substrate and electron acceptor for the denitrification process. The diffusion coefficient of $N_2O$ in a wet soil differs from that in a dry soil; it increases with a decrease in soil moisture content (Cho et al. 1997). Nitrous oxide is the dominant gas from the nitrification processes at a relatively dry soil water content (WFPS <60%). In contrast, at higher moisture (WFPS > 80%) content, $N_2$ is usually the prevalent gas released in the denitrification process (Ding et al. 2007). Thus, in a complete denitrification process under wet condition, the amount of $N_2$ released into the atmosphere will likely be greater than $N_2O$ as the later is used as electron acceptor after nitrate have been exhausted in the soil (Cho et al. 1997). Various factors affect the availability of water in the soil: environmental factors such as precipitation in the form of rainfall, snow, dew and irrigation; soil temperature; soil physicochemical properties such as soil texture, bulk density, porosity, soil structure, organic matter content; vegetal cover; crop management such as cover crop, mulching, crop rotation, and perennial cropping systems.

### 1.3.3 Oxygen

Oxygen is a major regulator of decomposition, nitrification and denitrification processes in soil. Nitrification is an aerobic process which requires oxygen for the conversion of ammonium to nitrate, while denitrification is an anaerobic process in which oxygen inhibits denitrifying enzymes (Hofstra and Bouwman 2005). Decomposition can be aerobic or anaerobic, although aerobic decomposition is more frequent than anaerobic decomposition. Denitrification was initially considered to be an obligate respiratory process, but studies have shown that denitrification can also be carried out by aerobic organisms (Bollmann and Conrad 1998; Su et al. 2015; Thomas et al. 1994). In aerobic microbial respiration, oxygen is preferred to nitrate as a terminal electron acceptor. In the absence of oxygen, nitrate is used as an electron acceptor. Some microorganisms are active only in the absence of $O_2$ and they are true or obligate anaerobes. In contrast, facultative anaerobes can survive under aerobic and anaerobic conditions (Cho et al. 1997a). Oxygen affects the gene and enzyme activity of the denitrifying organisms (Thomas et al. 1994).

The soil is made up of solids and pore spaces. Both air and water compete for the pore spaces in the soil. The rate of diffusion and dissolution of oxygen in soil water is low compared to soil air (Cho et al. 1997b). Atmospheric air has about 21% of oxygen whereas water has less than 1% dissolved oxygen. In the presence of water, the air is displaced from the soil system, thus increasing the water content of the soil is a way of displacing oxygen from the soil. Any agricultural practice that will control the moisture content of the soil will eventually control the amount of oxygen in the soil which will, in turn, regulate microbial activities and greenhouse gas flux from soil.

### 1.3.4 Organic Carbon

Carbon is essential for the respiration of microbes in soil and is used for energy production. Carbon is a constituent of the structural makeup of microbes. Organic carbon acts as an electron donor (Thomas et al. 1994). The carbon content of substrates will affect its carbon to nitrogen ratio. True nitrifiers are autotrophs that use N from inorganic sources while denitrifying microbes are heterotrophs. Thus, they obtain carbon from organic carbon sources. Hu et al. (2009) reported that increasing the C:N ratio of substrate increased denitrifying communities more than nitrifiers. The breakdown of carbon provides the ATP required by microorganisms through the process of respiration. Water-soluble carbons are easily decomposable by microorganisms in soil and they provide the necessary substrate for nitrifying and denitrifying organisms (Miller et al. 2012). Labile carbon from simple sugars such as glucose is easily decomposed unlike complex sources such as plant residues. Shannon et al. (2011) observed that the addition of glucose-C significantly increased the activity and abundance of denitrifiers compared to soil with no glucose.

### 1.3.5 Available Nitrogen

Soil nitrogen sources include input from fertilizer, manure, plant debris, lysis of microbial cells, atmospheric fixation, and other nitrogen fixation sources. Shortly after the addition of manure or other organic N sources to the soil, it is mineralized, releasing nitrogen into the soil in the form of ammonium. The ammonium is subsequently taken up by plant or nitrified to nitrate. Ammonium nitrogen is the basic substrate for the nitrification process while nitrate or nitrite is required for the denitrification process. Increasing soil nitrate content will likely increase denitrification if other conditions are favourable in soil. Hayatsu et al. (2008) pointed out that in the presence of nitrate and nitrite and limited supply of oxygen, denitrification activities of bacteria are stimulated. Nitrogen content increases the ease with which organic materials can be decomposed in soil. Low C:N ratio materials contain a higher concentration of nitrogen; thus, they can easily be decomposed by microorganisms. This will increase microbial activity and subsequently, greenhouse gas flux.

### 1.3.6 pH

The pH of the soil is a measure of its acidity or alkalinity. The optimum pH for crop production ranges from 6 to 8 in soil. In general, microbial activity tends to increase linearly with pH from 4 to 8 or up to the optimum pH (Čuhel and Šimek, 2011), as such $CO_2$ emission is expected to increase too. Acidic conditions have been found to inhibit activities of microbial communities, which also affect the rate of greenhouse gas emission under this condition.

## 1.4 Crop and nutrient management practices to mitigate nitrous oxide emission from agricultural soil

### 1.4.1 Fertilizer and manure management

Nitrogen which can be obtained from manure and fertilizer applications is an essential nutrient required for crop growth and development. If this crop nutrient is not effectively managed, it can be lost in form of nitrous oxide emissions. The 4R nutrient management strategy: right timing, right placement, right rate and right source (Robertson et al. 2013) can be adopted by farmers to mitigate nitrous oxide emission from organic amendment or fertilizer application. Right timing will consider application relative to the presence of plants that will take up the nutrient. Spring application may be a better choice compared to fall applications (VanderZaag et al. 2011). However, if farmers are considering labour availability, cheap fertilizer resources and efficient time utilization, late fall application may be accompanied by inhibitors (Tiessen et al. 2006; Lasisi et al. 2019). Fertilizer can also affect soil pH, which in turn affects the rate and product of nitrification and denitrification processes. Right placement involves a consideration between banding, surface broadcast, incorporation and other methods of fertilizer placement. Banding fertilizer in a concentrated form will create a toxic environment for microorganism thus reducing their activity. When fertilizers are incorporated into the soil, more contact area is created for microorganisms, which eventually could accelerate nitrification and denitrification in soil (Tiessen et al. 2006).

Rates of fertilizer application or organic amendments have been reported to have an influence on nitrification/denitrification processes in soil and subsequently greenhouse gas emission (Roy et al. 2014). High rates of fertilizer application in a wet environment and under favourable temperature will promote nitrification/denitrification in soil and subsequently greenhouse gas flux. The N from manure applied to soil that is available to crop usual varies with the source, its dry matter content, organic and inorganic N content among other factor. The best way to reduce greenhouse gas emissions is to match crop uptake with fertilizer supply (Roy et al. 2014). This thesis explores the $N_2O$ implication of applying LPM and its equivalent urea N to annual crops.

The right source may consider using nitrate fertilizers vs. ammonium fertilizers, or inorganic fertilizer vs. organic amendment such as liquid or solid manure. Manure increases the amount of available nitrogen and carbon in the soil. Soluble carbon and volatile fatty acids are present in manure that stimulate nitrification/denitrification and increase the activity and abundance of nitrifiers/denitrifiers in the soil (Miller et al. 2012). One may argue that solid pig manure increase soil carbon availability in soil compared to liquid pig manure and inorganic fertilizers, thus providing carbon sources to microbial communities (Miller et al. 2009), but do these N sources actually differ in $N_2O$ emissions when applied to cropped land? This thesis answers the question of how LPM differs from SPM in terms of $N_2O$ emission when applied to perennial and annual crops.

### 1.4.2 Crop management

Crop rotation, when combined with forage legumes or perennial forage grasses has proven to be effective in mitigating greenhouse gas emissions. Taylor et al. (2013) observed a net greenhouse gas reduction of 480 kg C/ha/yr under hay-pasture cropping system compared to continuous annual crops. Crop rotation can be set up to take advantage of soil moisture and N recycling in soil by choosing appropriate crop sequence (Saskatchewan Agriculture and Food (SAF) 2005). Considering fibrous-rooted crops such as timothy and orchard grasses in crop rotations can help in recycling plant nutrients and making it available for subsequent crop while improving the soil structure for good water holding capacity (Adesanya et al. 2016). In a study on $N_2O$ and $CO_2$ during perennial forage establishment Maas et al. (2013) reported a net greenhouse gas reduction when perennial forage hay was included in annual crop rotation. Jefferson et al. (2013) also reported significant yield increase and N uptake of barley following termination of perennial forage grasses. One challenge is having an estimate of greenhouse gas emission during the disruptive phase when perennial forage grasses are converted to annual crops most especially when pig manure is continuously applied.

Tillage operations are agriculture practices that help to prepare the soil for planting. There are various forms of tillage practices: conventional, reduced, conservation, and no-till (Bessou et al. 2011). According to the literature, there are contrasting views on the effect of short term tillage on greenhouse gas emission.  No-till and reduced tillage may be used to control greenhouse gas emission compared to conventional tillage (Bayer et al. 2016). During conventional tillage operations, soil is mixed together, thus increasing the contact of microorganisms with organic materials in the soil, eventually, nitrification and denitrification rates are increased (Mei et al. 2018). Sometimes, compaction zones and layers may be created in the process, depending on the kind of equipment used. This may create impervious layers in the soil, leading to reduced percolation and infiltration, thus creating waterlogged conditions on the field (Logan et al. 1991). Tillage operations may also increase erosion in the soil. During the period immediately following tillage, when no plant is growing on the soil, the nutrient may be washed off by erosion or runoff. Tillage may reduce the amount of moisture stored in the upper soil surface, creating a dry condition. This is so because the evaporation rate is increased as drier air can infiltrates the soil (Oertel et al. 2016).

### 1.5 Modelling nitrogen dynamics in soil and environment

A model is a conceptualized system comprising of different components developed to represent and understand the real world. A process-based model simulates physical and biogeochemical processes involved (Adams et al. 2013). Process-based models are efficient ways of estimating greenhouse gas fluxes from agricultural systems as they can be used to identify efficient management practices that will mitigate GHGs emissions. Environmental factors such temperature and precipitations that interact with ecological derivers in soil-plant systems are incorporated into process-based model simulations. The ecological drivers and processes are assigned mathematical equations to solve for variables that influence GHG from agricultural systems.

There are several models available for estimating carbon and nitrogen dynamics in manured fields. Common ones are DeNitrification DeComposition model (DNDC) (Li et al. 1992) DAilY version of CENTury model (Daycent) (Parton et al. 1998), NLOSS (Riley and Matson 2000), Root Zone Water Quality Model (RZWQM), Water and Nitrogen Management model, WNMM (Li et al. 2007), Environmental Policy Integrated Climate, EPIC (Roloff et al. 1998), and Simulateur mulTIdisciplinaire pour les Cultures Standard, STICS (Brisson et al. 2003). Of these models, DNDC is the most versatile, owing to its ability to model crop and nutrient managements from all facet of agroecosystem. There have been recent developments in the DNDC model with the latest stable version being DNDC 9.5. A number of branches have also sprung up from the DNDC based on different regional and ecological needs. DNDC v.Can is a regional version of the DNDC adapted for the Canadian agroecological climates, improving upon the current strength of the DNDC 9.5 (Smith et al. 2020; Dutta et al. 2017). As models are developed, there is need for constant testing and evaluation. Moreover, there is little or no study that has evaluated the recent development in DNDC v.Can on estimating $N_2O$ fluxes from perennial forage grasses and annual crops amended with pig manure in the prairie region of Canada (He et al. 2020). In this thesis I assessed the recent development in the DNDC v.Can in estimating soil moisture and $N_2O$ flux from perennial forage grasses and annual croplands amended with pig manure.

### 1.6 Study objectives

The overall objective of this thesis was to determine the best crop and nutrient management practices with respect to annual and perennial forage grasses amended with pig manure and inorganic fertilizer that will mitigate nitrous oxide emission from agricultural soils. The following were the specific objectives of the study 1.) To evaluate the impact of converting perennial forage grasses receiving continuous application of pig manure to annual crops on $N_2O$ emission and soil nitrogen availability. 2.) To assess the $N_2O$ implication of applying constant volume of LPM and its equivalent N as urea fertilizer to cropped land. 3.) To evaluate the ability of the DNDC model to simulate soil moisture and $N_2O$ fluxes from liquid and solid pig manure applied to annual crops and perennial forage grasses.

## 1.7 Thesis organisation

This thesis reported on measurement and simulations of nitrous oxide fluxes from perennial forage grasses and annual crops amended with liquid pig manure, solid pig manure and inorganic fertilizer. There are five chapters in the thesis. Chapter one introduces the thesis with a background on greenhouse gas and nitrous oxide emissions from agricultural soils. Chapters two to four were written in manuscript format. Chapter 2 described $N_2O$ flux from the plow down of perennial forage grasses and compared it with those of annual plots both receiving annual application of solid and liquid pig manure. The study was carried out at the Ian Morrison Research Station, Carman, Manitoba, Canada. Chapter three was on a study carried out on a loamy sandy soil seeded to wheat or barley in Carberry, Manitoba. The study reported on $N_2O$ fluxes from liquid pig manure and inorganic fertilizer (urea) applied to annual cropped land. Chapter four uses the data from the Carman site to simulate nitrous oxide fluxes and soil moisture from perennial forage grasses and annual plots that were amended with LPM and SPM using the DNDC model. Chapter five is an overall synthesis of the thesis; it presents a general summary of the findings with a discussion of connections between individual manuscript, its practical implications, and recommendations for further studies.

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# 2. SOIL NITROUS OXIDE EMISSIONS ASSOCIATED WITH CONVERSION OF FORAGE GRASS TO ANNUAL CROP RECEIVING ANNUAL APPLICATION OF PIG MANURE

## 2.1 Abstract

The disruptive land-use change during forage grass conversion to annual crop can be critical for determining nitrous oxide ($N_2O$) emissions, but this is an understudied period. I measured soil $N_2O$ fluxes (using closed static vented chambers) together with potential environmental drivers of these fluxes from liquid pig manure (LPM) and solid pig manure (SPM) applied to an annual crop (ANN) and perennial forages (FPP) that was converted to annual crop. Unamended plots were used as a control (CON). The results showed that in 2013, average soil nitrate-N was significantly higher on the recently converted perennial forage plots (ranging from 19 to 83 mg N kg$^{-1}$) than the continuous annual plots (16 to 35 mg N kg$^{-1}$). The recently converted perennial forage system produced three times greater $N_2O$ than the continuous annual system, which is likely a result of accelerated N mineralization from the accumulated soil organic matter (from 2009 to 2012) and grass residues of the recently killed forage grasses. However, during the second year of the study, when the FPP plots were reseeded to perennial grasses, the system emitted 30 % less $N_2O$ than the ANN system. These results suggest that including perennial forage grass in rotation with annual crops can provide N-saving and climate change mitigation benefits; however, some of the N stored in the soil would be lost when the perennial grass plots are cultivated to grow annual crops.

**Keywords:** nitrous oxide; termination; perennial forage grasses; pig manure; greenhouse gas

## 2.2 Introduction

Nitrous oxide ($N_2O$) is the main greenhouse gas (GHG) emitted from cropped land. It is mostly emitted from agricultural soils when fields are treated with nitrogen-based fertilizers and manure to improve annual and forage crop yields. $N_2O$ emitted from agricultural soils is particularly important because it has a 100-year global warming potential effect that is up to 265 times greater than that of carbon dioxide (IPCC 2014). According to Environment Canada (2014a), agriculture accounted for 10% of $CO_2$-equivalent GHGs produced in Canada in 2012. On a global scale, agriculture contributed 24% to direct GHG emissions in 2010 (IPCC 2014). It is often acknowledged that including perennial forage crops in rotation with annual crops is a useful strategy to reduce GHG emissions, particularly $N_2O$ from agriculture (Asgedom and Kebreab 2011). However, soil $N_2O$ emission associated with the disruptive land-use change during perennial forage crop conversion to annual crops could be important but has remained an understudied source of agricultural GHG emissions.

Pasture mixtures containing perennial forage crops, such as Timothy grass (*Phleum pretense L.*) and orchard grass (*Dactylis glomerata L.*), are efficient in scavenging available soil nitrogen (Jones et al. 2005). The extensive rooting system of perennial forage grasses can bind soil together and create a large surface area to intercept soil nutrients (Popay and Crush 2010). Perennial grassland systems are known to be large stores of soil organic matter (SOM), at least in the topsoil layer that may become susceptible to accelerated mineralization, nitrification, and denitrification once they are converted to annual crops. In a 2-year rotation experiment, Maas et al. (2013) found that $N_2O$ emission from annual crops ($7.8 \pm 0.7$ kg N $ha^{-1}$) was four times greater than that from perennial forage grasses ($1.8 \pm 0.7$ kg N $ha^{-1}$).

Perennial forage grasslands can be converted to annual crops for economic considerations (Taylor et al. 2013). In other cases, they are grown in rotation with annual crops (Maas et al. 2013; Jefferson et al. 2013) on the Canadian Prairie such as wheat, barley, or canola. Although it is not a common practice to have a large area of grasslands converted to annual crops, the practice does take place (Fraser and Amiro 2013). Native grasslands are being transformed to annual cropland for agricultural production. Also, livestock producers in the prairie region apply manure to forage crops that are planted in rotation with annual crops that are fed to animals. Perennial forage grasses offer the benefit of increased grain yield to succeeding annual crops following their termination (Asgedom and Kebreab 2011). However, the soil may lose organic matter and nitrogen levels may decline after perennial forage grasslands are converted to annual crops (Fraser and Amiro 2013). Drewer et al. (2016) reported that plowing managed temperate grassland increased $N_2O$ fluxes. Mielenz et al. (2016) used a modeling approach to evaluate mitigation strategies for $N_2O$ emissions from cropping systems after conversion from pastureland. They predicted $N_2O$ emissions to be high after land-use change from pasture to arable cropping.

With a trend of increasing pig production in Canada (Statistics Canada 2017), annual pig manure production has also increased. Land application of pig manure is the most economical and environmentally acceptable method of utilizing the manure. Pig manure is a source of plant nutrients, particularly nitrogen. Pig management systems produce two types of manure: liquid pig manure (slurry) or solid pig manure (straw beddings mixed with urine and feces). Very few studies have reported estimates of $N_2O$ fluxes from either pig manure applied to soil following the termination of perennial forage grasses.

A few studies have monitored $N_2O$ emissions from pig manure applied to perennial forage grasses. Tenuta et al. (2010) reported high $N_2O$ emissions from a single spring application of LPM compared to split application of LPM and control unamended plots. They recommended a split application rather than a single spring application to reduce $N_2O$ emission. Gao et al. (2014) reported increased $N_2O$ emission following the addition of pig slurry to perennial forage grasses, which they attributed to increases in soil nitrogen and soil moisture content. Rochette et al. (2008) observed no clear distinction between $N_2O$ emission from SPM and LPM. Nikièma et al. (2016) concluded that SPM would better mitigate $N_2O$ emission compared to LPM, especially under conditions that favour denitrification, because the emission intensity and emission factor for SPM were significantly lower than those from LPM.

There is a dearth of information on the $N_2O$ emission implication of converting perennial forage grasses into annual crops that are fertilized using pig manures. This study aimed at evaluating the impact of the conversion phase of a 4-year perennial forage cropping system, receiving annual applications of pig manure to annual crops on $N_2O$ emission and soil nitrogen availability. I hypothesized that the conversion of a prior permanent grassland-use to an annual cropping system would enhance $N_2O$ emissions due to accelerated N mineralization from both SOM and grass residues from the newly killed perennial grasses. I also hypothesized that converting the new annual crop back to a perennial forage system will result in lower soil $N_2O$ emissions relative to a continuous annual cropping due to greater ability of the perennial grasses to uptake mineralized N from SOM and N addition to the soil from the pig manure.

## 2.3 Materials and Methods

### 2.3.1 Experimental site

The field site for this study was at the University of Manitoba Ian N. Morrison Research Farm in Carman, Manitoba, Canada (49° 29.619'N, 98° 2.204'W, 266.1 m a.s.l.). Over a 30-year period (1981-2010**)**, the farm average annual precipitation was 545 mm (Environment Canada, 2014a). The soil is a well-drained sandy loam of Hibsin series, an Orthic Black Chernozem in the Canadian classification system (Michalyna et al. 1988), with an average bulk density of 1.2 Mg $m^{-3}$ and pH 6.5 (1:2 water suspension) to a depth of 15 cm (Adesanya 2015; Adesanya et al. 2016).

The experiment was a split-plot design, with the two original cropping systems (annual and perennial) as the main plots and three manure treatments (liquid pig manure (LPM), solid pig manure (SPM), and control of no manure addition (CON) as subplots, with all treatments, replicated four times. Each plot was 10 m by 10 m in size. From 2006 to 2009, this site had been a mixture of three forage crops, Alfalfa, timothy grass and orchard grass in ratio 50:35:15 with no nutrient supplement (Nikièma et al. 2016; Karimi et al. 2017). In 2009, alfalfa was eliminated from the mixture by spraying with herbicide Lontrel (clopyralid, Dow AgroSciences Canada Inc.) and MCPA (2-methyl-4-chlorophenoxyacetic acid, Nufarm Agriculture Inc) at a rate of 0.84 l $ha^{-1}$ and 0.98 l $ha^{-1}$ respectively, while the proposed annual plot was sprayed with Round-up herbicide (Isopropylamine salt of glyphosate, Bayer Inc.) at a rate of 5.5 l $ha^{-1}$. Since 2009, both LPM and SPM plots have received pig manure as N supplement similar to those reported in this study, while CON plots have been left unamended. The applied manure rates aimed at meeting 150 kg N $ha^{-1}$ on ANN and 140 kg N $ha^{-1}$ on FPP depending on target crop yield and residual soil nitrate (60 cm soil depth) measured from the preceding fall period. A detail of the manure application rate during the 2009 to 2012 period have been reported by Nikièma et al. (2016) and Karimi et al. (2017).

Also, since 2009, the annual plots (ANN) have been in a barley (*Hordeum vulgare* 'Tradition')-rapeseed, canola hybrid (*Brassica napus* L. 'Liberty Link', Invigor L140P) rotation. The former perennial plots (FPP) were left with a mixture of timothy grass (*Phleum pratense* L. 'Promesse') and orchard grass (*Dactylis glomerata* L. 'AC Nordic') planted in a ratio of 68% to 32%, respectively. In fall 2012, FPP plots were terminated by plowing using a tandem disc plow to a depth of 10 cm for the start of the current study. In spring 2013, both FPP and ANN plots were cultivated and seeded to canola on 11$^{th}$ June 2013. In the fall of 2013, after harvesting of canola, the FPP plots were reseeded to timothy and orchard grasses on 23$^{rd}$ of September 2013, although this was late seeding, the grasses performed well without adverse effect before winter set-in in November of that year. In the spring of 2014, the ANN plots were seeded to barley on the 6$^{th}$ of June 2014. One-year rotation of FPP to ANN may seem short and unorthodox, but I do not anticipate that the nitrogen from the grass residue will persist longer than one-year. The seeding rates for canola and barley were 8 and 108 kg ha$^{-1}$, respectively, while the seeding rate for timothy and orchard grasses mixture was 8.4 kg ha$^{-1}$.

The liquid pig manure was collected from an earthen lagoon on a farmer's farm near Steinbach, Manitoba, while the solid pig manure was collected from a compost pile at the National Centre for Livestock and the Environment of University of Manitoba, Glenlea, Manitoba, Canada. The collections were close to the time of manure application each year, usually within a week. Sub-samples of the manures were analyzed for moisture, total N and ammonium nitrogen (Table 2.1). Manure addition rates were calculated based on the N requirement of each crop (Manitoba Agriculture Food and Rural Initiatives 2007), taking into consideration residual soil nitrate (Table 2.2) and expected crop yield. It is an acceptable practice in this region to assume that 25% of applied ammonium N to ANN will be lost through volatilization when manure was applied and incorporated on the same day. In comparison, 50% of applied ammonium N will be lost through volatilization on FPP when manure was surface applied without incorporation, a reference to this can be found in the report of the Prairie Provinces' Committee on Livestock Development and Manure Management (2004). The committee also assumed that only 25% of applied organic N in manure would be available for plant use in the first year of application. Manitoba Agriculture Food and Rural Initiatives (2007) assumed that previous fall extracted N (60 cm soil depth) determines how much of N will be available in the following growing season. The higher the soil nitrate N, the higher the chances of meeting crop N need. As such, an empirical table has been developed to categorize soil N, ranging from very low (VL) to very high (VH) depending on crop type. The target yield used in estimating N requirements was 2.1, 4.6 and 7.4 Mg $ha^{-1}$ for canola, barley and forage mixture respectively, which is usually based on average provincial crop yield in the preceding growing season.

Due to the low residual soil $NO_3^-$-N from FPP in 2013 more manure-N was applied to these plots to meet the target yield. Also, no N credit was ascribed to the plow-down forage mixture plots. In 2013, manure was applied to all plots on 11 June and incorporated on the same day to a depth of 10 cm using a tandem disc plow. In 2014, manure was applied to all plots on 5 June; it was incorporated on 6 June for ANN plots but left on the soil surface for FPP plots.

**Table 2.1** Chemical composition of the liquid (LPM) and solid (SPM) pig manure used for the experiment in 2013 and 2014.

| Year | Manure | Dry Matter | Total N | $NH_4^+$ | Organic N | C:N Ratio |
|---|---|---|---|---|---|---|
| | | (kg $L^{-1}$ or kg $kg^{-1}$) | (mg $L^{-1}$ or mg $kg^{-1}$) | | | |
| 2013 | LPM | 0.07 | 5834 | 3509 | 2325 | 5 |
| | SPM | 0.25 | 7278 | 273 | 7005 | 15 |
| 2014 | LPM | 0.01 | 1637 | 1351 | 286 | 4 |
| | SPM | 0.23 | 7064 | 1350 | 5714 | 14 |

**Note**: Unit for LPM manure is expressed as kg $L^{-1}$ and mg $L^{-1}$ for dry matter and nitrogen contents respectively, while that of SPM manure is expressed as kg $kg^{-1}$ and mg $kg^{-1}$ for dry matter and nitrogen contents respectively.

**Table 2.2** Residual soil nitrate-nitrogen and manure application rates from the liquid pig manure (LPM) and solid pig manure (SPM) to the annual (ANN) and perennial forage grass plots (FPP) in 2013 and 2014

| Year | Cropping System | Manure Treatments | Residual Soil $NO_3^-$–N | Applied Total Available N[a] | Target Plant Available N Expected | Total Applied Manure[b] | Applied Organic C | Applied Total $NH_4^+$ and $NO_3^-$ [c] | Applied Organic N[c] | Applied Total N [c] |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | kg N ha$^{-1}$ | kg N ha$^{-1}$ | kg N ha$^{-1}$ | L ha$^{-1}$ or kg ha$^{-1}$ | kg C ha$^{-1}$ | kg N ha$^{-1}$ | kg N ha$^{-1}$ | kg N ha$^{-1}$ |
| 2013 | ANN (Canola) | LPM | 60 | 56 | 145 | 19720 | 618 | 69 | 46 | 115 |
| | | SPM | 70 | 41 | 145 | 21000 | 2280 | 6 | 147 | 153 |
| | | CON | 28 | | | | | | | |
| | FPP (Canola) | LPM | 7 | 148 | 162 | 52460 | 1643 | 184 | 122 | 306 |
| | | SPM | 10 | 143 | 162 | 73000 | 7927 | 20 | 511 | 531 |
| | | CON | 8 | | | | | | | |
| 2014 | ANN (Barley) | LPM | 50 | 50 | 150 | 46470 | 288 | 63 | 13 | 76 |
| | | SPM | 52 | 47 | 150 | 20250 | 2057 | 27 | 116 | 143 |
| | | CON | 18 | | | | | | | |
| | FPP (Timothy+Orchard) | LPM | 88 | 53 | 140 | 48260 | 299 | 65 | 14 | 79 |
| | | SPM | 102 | 38 | 140 | 16000 | 1626 | 22 | 91 | 113 |
| | | CON | 27 | | | | | | | |

[a]Total Available N is calculated as (Manure $NH_4^+$-N × (100% − % Volatilization loss)) + 25% Manure Organic N (Prairie Province’s Committee on Livestock Development and Manure Management 2004).
[b]LPM is measured in L ha$^{-1}$, while SPM is measured in kg ha$^{-1}$.

[c]Applied Total N does not exclude N loss to the environment, nor does it exclude organic N that will not be available each year.

### 2.3.2 Nitrous Oxide Flux Measurements

I used the static vented chamber technique for collecting $N_2O$ fluxes. Three chambers were installed in each plot. The chambers were made up of polyvinyl chloride (PVC) collar that was 20.3 cm in diameter and 10 cm in height. In both years, 2013 and 2014, gas flux measurements began in May and ended in October. Before the manure application each year, gas flux measurement was carried out to determine background $N_2O$ flux. Following manure application and seeding, $N_2O$ emissions were measured two times a week during the first three weeks. The sampling frequency was then reduced to once a week during the next four weeks, fortnightly for the next month, and then once a month for the rest of the sampling period. Gas samples were collected from the headspace of each chamber, as described by (Nikiema et al. 2016). Following the closure of the chamber, a 20 ml syringe was used to draw gas from the headspace at 15 minutes interval during a 45-minute period. Each gas sample was immediately transferred into a 12-ml Exertainer vial (Labco Canada). The concentration of $N_2O$ of gas samples was determined using a Varian CP-3800 gas chromatograph analyzer (CP-3800, Varian Canada, Mississauga, ON). The gas chromatography was fitted with an electron capture detector. Standard $N_2O$ gases were prepared by dilution of a reference gas from Praxair Canada incorporation, which was then calibrated for the estimation of unknown samples. During the analysis, blank, standardized, and reference samples were included at intervals for quality assurance and control. Any sample set that has its reference greater than 5% of the expected value, the whole set is rejected and rerun to identify the error source.

The gas flux rates were calculated using the revised model of Hutchinson and Mosier (1981) (HM), as described by Pedersen et al. (2010) in HMR, an add-on package in R software (The R Foundation) available at (https://cran.r-project.org/package=HMR). A plot of gas concentration against the time interval describes the curve for estimating the flux. Depending on the fit of the curve, the software recommends one of the following models, non-linear, linear, or no flux. In the current study, the recommendations were usually accepted except for a few cases of no flux in which the linear model was used. An example of such a situation is when the first 3 data values follow a linear trend but not the last value, which may fall to almost the initial value. I try to observe the plot of concertation against time from the package and see if it fits a linear graph or not. More so, rather than filling with zero of no flux, accepting the linear model gives a neutral output as such, the number of zero fluxes is reduced, and this allowed for better data analysis. Calculated fluxes were scaled to g N $ha^{-1}d^{-1}$. Linear interpolation gap-filling function was adopted to estimate fluxes for days that were not sampled. Cumulative growing season fluxes were estimated by summing up measured and gap-filled fluxes from starting period of sampling in May to end of the sampling period in October each year.

### 2.3.3 Soil Sampling and Analysis

Soil samples from 0-10 cm depth were taken around each collar at each sampling period using a 4 cm width Dutch auger. These samples were analyzed for gravimetric water content, and 2 M KCl extractable ammonium nitrogen ($NH_4^+$-N) and nitrate-nitrogen ($NO_3^-$-N) concentrations (Li et al. 2012; McTaggart et al. 1993) using a SEAL Discrete Analyser (AQ2®, SEAL Analytical Inc., WI).

### 2.3.2 Ancillary Data

Weather data, including air temperature and precipitation, was obtained from a nearby Environment Canada weather station, 200 m away from the study site (Environment Canada 2014a). On each gas sampling occasion, soil temperature was taken at 0-2.5 cm depth around every gas chamber using a Fischer's Scientific soil thermometer (Thermo Fisher Scientific Inc., MA). In both 2013 and 2014, at the end of the growing season, plant samples were harvested by collecting four-quadrant samples per plot with each quadrant measuring 50 cm by 50 cm. Row count within each quadrant was taken into consideration, usually three rows for the annual crops. Plant samples were cut at the base just above the ground level using a sickle. The four-quadrant samples per plot were bagged together and dried at 35 °C for 2 weeks in a drying room. The dried samples of annual crops were threshed for grain, while only the biomass of forage grasses were weighed, and yield scaled to kg $ha^{-1}$.

### 2.3.4 Nitrous oxide emission factor and emission intensity

The nitrous oxide emission factor and emission intensity per plot were calculated using the following formulas:

$$\text{EF\_Total\_N} = \left(\frac{\sum(\text{N}_2\text{O}-\text{N})\ \text{Amended soil} - \sum(\text{N}_2\text{O}-\text{N})\ \text{Control}}{\text{Manure Applied Total N}}\right) \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (1)$$

$$\text{EF\_Total\_Available\_N} = \left(\frac{\sum(\text{N}_2\text{O}-\text{N})\ \text{Amended soil} - \sum(\text{N}_2\text{O}-\text{N})\ \text{Control}}{\text{Total Available N}}\right) \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

$$\text{EF\_Target\_N} = \left(\frac{\sum(\text{N}_2\text{O}-\text{N})\ \text{Amended soil} - \sum(\text{N}_2\text{O}-\text{N})\ \text{Control}}{\text{Target N}}\right) \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (3)$$

Where EF_Total_N, EF_Total_Available_N and EF_Target_N are emission factors calculated based on Total N, Total Available N and Target N respectively.

$\sum(\text{N}_2\text{O}-\text{N})\ \text{Amended soil}$ = Cumulative $N_2O$–N from the amended treatments (kg N $ha^{-1}$).

$\sum(\text{N}_2\text{O}-\text{N})\text{Control}$ = Cumulative $N_2O$-N from the control plots (kg N $ha^{-1}$).

Manure applied total N = Total manure nitrogen applied to amended plot (kg N $ha^{-1}$).

Total Available N = Amount of manure applied N that will be available for plant use, including nitrate, ammonium and potentially mineralizable N during the growing season, excluding gaseous losses during application (kg N $ha^{-1}$). It is calculated as (Manure $NH_4^+$-N × (100% − %

Volatilization loss)) + 25% Manure Organic N (Prairie Province's Committee on Livestock Development and Manure Management 2004).

Target N = Amount of plant nitrogen expected to be available to plant both from residual soil nitrogen and potentially mineralizable N during the growing season (kg N ha$^{-1}$).

$$\text{Emission intensity} = \frac{\sum(N_2O-N)}{(\text{Yield})} \qquad \text{.................................................} \ (4)$$

Where $\sum$ ($N_2$O-N) = cumulative $N_2$O-N from the treatment (kg N ha$^{-1}$), Yield = grain or biomass yield from the treatment (Mg ha$^{-1}$)

### 2.3.5 Statistical analysis

The data were subjected to statistical analysis using SAS® software package (SAS Institute Inc., Cary, NC). The PROC UNIVARIATE procedure was used to test the data for normality. It was observed that all the dependent variables conformed to a lognormal distribution except for soil gravimetric water content (GWC) and soil temperature that were normally distributed. As such, lognormal distribution was specified for the PROC GLIMMIX procedure used in analyzing the data except for the two variables (soil gravimetric moisture content and soil temperature). The PROC GLIMMIX procedure of SAS® for the repeated measure was used to perform the analysis of variance as split-plot design with two cropping systems as the main factor (ANN and FPP) and three manure treatments as the subplots (CON, LPM, and SPM). Data were analyzed on a yearly basis, 15 sampling dates were analyzed in 2013, while in 2014, 16 sampling dates were considered. The fixed factors were cropping system, manure treatment, and sampling date in the PROC GLIMMIX procedure. The three chambers in a plot were nested within treatments. There were four blocks as random factors. A significant difference was accepted at a probability level of 0.05 using the Tukey-Kramer method.

## 2.4 Results

### 2.4.1 Environmental Data

Annual precipitation was greater in 2014 than in 2013 by 17% (64 mm) as shown in Table 2.3 (Environment Canada 2014a). In 2013, the annual precipitation was 366 mm compared to 430 mm in 2014. These values are below the long-term average of 545 mm for this region. Similarly, rainfall during the growing season from May to October in 2013 (313 mm) was lower than that in 2014 (350 mm), which were both lower than long term normal of 412 mm during this period. However, in 2013, greater than normal precipitation was received in May while June, July and August were drier than normal. As well, in 2014, greater than normal rainfall was observed mainly in June and August while May, July and September were drier than normal. Average temperatures were above 0 °C from May to October in both years (2013 and 2014), with the highest mean monthly temperature occurring between July and August in both years (17.8 °C to 18.7 °C). Within this period, the lowest mean temperatures occurred in October in both 2013 (4.7 °C) and 2014 (7.0 °C).

**Table 2.3** Total monthly precipitation and mean monthly temperature for the study period (2013 and 2014) and long-term average (1981-2010) at the experimental site in Carman. Data source: ECCC (2014a)

| | Total Precipitation (mm) | | | Mean Temperature (°C) | | |
|---|---|---|---|---|---|---|
| Month | Climate normal (1981-2010) | 2013 | 2014 | 30-year average | 2013 | 2014 |
| January | 18±10 | 5.2 | 14.7 | -15.3±4.4 | -16.0 | -18.2 |
| February | 16±24 | 4.9 | 3.9 | -11.8±4.2 | -14.1 | -18.5 |
| March | 21±26 | 18.2 | 6.4 | -5.3±3.4 | -11.9 | -11.0 |
| April | 39±18 | 10.3 | 40.1 | 4.5±3.2 | -2.8 | 0.9 |
| May | 70±37 | 111.0 | 30.9 | 11.6±1.9 | 10.4 | 11.3 |
| June | 96±36 | 50.6 | 116.7 | 17.2±1.4 | 17.7 | 16.6 |
| July | 79±43 | 49.0 | 27.6 | 19.4±0.8 | 18.6 | 17.8 |
| August | 75±32 | 59.4 | 122.4 | 18.5±1.8 | 18.7 | 18.7 |
| September | 49±19 | 29.9 | 46.3 | 13.4±1.1 | 15.1 | 13.1 |
| October | 43±15 | 13.2 | 6.0 | 5.4±1.9 | 4.7 | 7.0 |
| November | 25±29 | 7.0 | 11.3 | -4.2±3.7 | -5.3 | -8.3 |
| December | 24±14 | 6.9 | 3.2 | -11.4±5.0 | -19.3 | -10.4 |
| Total or mean | 545±54 | 365.6 | 429.5 | 3.5±1.2 | 1.3 | 1.6 |

**Note:** Total refers to precipitation while mean refers to temperature. Values for a 30-year average are means ± SD.

### 2.4.2 $N_2O$ Emissions

In terms of temporal fluxes, background $N_2O$ emissions were low before manure application (< 4 g N $ha^{-1}d^{-1}$) on all the treatments in both years, although $N_2O$ flux was higher on the manure treated plots of FPP than the manure treated plots of ANN. In 2013, following manure treatment application, $N_2O$ fluxes increased gradually, reaching a peak after two weeks of N source application. The highest peak of $N_2O$ fluxes occurred on the LPM plots (Figure 2.1). The peak $N_2O$ emission from the LPM treated FPP plot was 351 ± 66 g N $ha^{-1}d^{-1}$ while LPM treated ANN plot had a peak emission of 177 ± 53 g N $ha^{-1}d^{-1}$ on June 27, 2013. After the 3rd week of manure application, $N_2O$ emission in manure treated plots declined to the levels measured in CON for the rest of the season (Figure 2.1). In 2014, the flux trend followed a similar pattern as in 2013; the base flux was low before the manure treatment application. Following manure application, the $N_2O$ flux increased until a peak is reached within one to two weeks after manure application. It is worth noting that the $N_2O$ fluxes in 2014 were low compared to 2013.

The statistical analysis of cumulative $N_2O$ flux showed that there was a significant interaction between cropping system and manure treatments in 2013 but not in 2014 (Table 2.4). The least-square means the significance of the main effects is shown in Table 2.4, while Table 2.5 shows the significance of interaction effects using Tukey-Kramer grouping. In 2013, following the conversion of the perennial forage grass plots to annual crop plots, the cumulative $N_2O$ flux from FPP was significantly greater than ANN ($p < 0.001$) on the manured plots (Table 2.4 and Table 2.5). For example, cumulative $N_2O$ flux from LPM of ANN was 1.2 kg N $ha^{-1}$ while equivalent flux from LPM of FPP was 3.7 kg N $ha^{-1}$ during the growing season of 2013 (Table 2.5). Since there was no significant interaction effect of cumulative $N_2O$ flux between cropping system and manure treatment in 2014; Table 2.4 showed that after the reestablishment of the terminated perennial forage grasses, cumulative $N_2O$ flux from ANN was significantly higher than FPP. Using Least Significant Difference (LSD), which is less conservative, will reveal the detailed difference between the means of the interaction effects as compared to Tukey-Kramer used in Table 2.5, which is more conservative, modest and reduce likely chances of error. Within each cropping system, $N_2O$ fluxes were not significantly different between the manure treatments. For example, during the growing season in 2013, cumulative $N_2O$ flux from LPM and SPM of ANN were 1.20 and 0.85 kg N $ha^{-1}$ respectively, which were not significantly different from one another (Table 2.5). In 2014, cumulative $N_2O$ flux from LPM and SPM of ANN were 0.52 and 0.59 kg N $ha^{-1}$ respectively, which were also not significantly different from one another.

Emission factors were calculated base on N from manure applied to soil as total N (EF_Total_N), total available N (EF_Total_Available_N) and target N (EF_Target_N) (Table 2.4 and Table 2.5). In 2013, nitrous oxide emission factor and emission intensity from FPP were two times greater than those of equivalent ANN. For instance, the emission factor from LPM of ANN was 0.67, whereas the emission factor from equivalent LPM of FPP was 1.09 kg N $kg^{-1}$ applied total N during this period. From Table 2.4, emission factors based on total available N and target N were also greater on FPP than ANN in 2013. On the other hand, in 2014, following the reestablishment of perennial forage grasses, emission intensity from ANN was significantly different from those of FPP (Table 2.4). This difference was not manifested in either the emission factors (Table 2.4 and Table 2.5) or the Tukey-Kramer grouping of interaction effects (Table 2.5). In both years, nitrous oxide emission intensity was not significantly different between SPM and LPM. Only in 2013 was EF_Total_N and EF_Target_N different between LPM and SPM (Table 2.4).

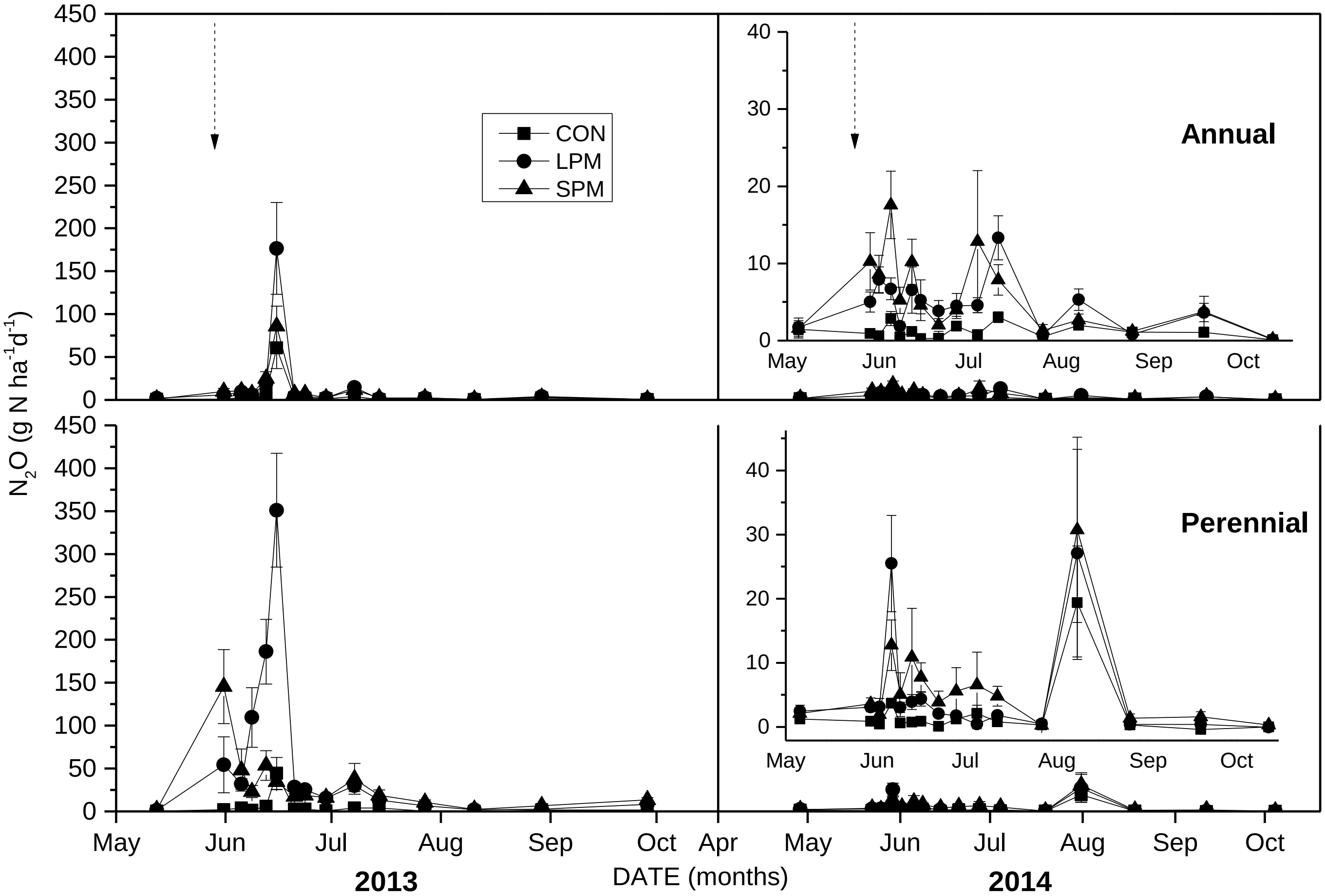


**Figure 2.1** Daily $N_2O$ flux during the growing season in 2013 and 2014 on ANN and FPP plots amended with liquid (LPM) and solid (SPM) pig manures. Arrows indicate the date of manure application (11/June/2013 and 09/June/2014).

### 2.4.3 Soil Moisture and Soil Temperature

Daily soil moisture distribution pattern during the growing season of 2013 and 2014 is presented in Figure 2.2. There was a significant interaction between the time of sampling, cropping systems and type of manure on the soil water content in 2013 ($p = 0.015$). The soil moisture gets saturated or close to saturation in June, whereas in early August, the soil moisture was reduced to a minimum level before increasing again at the end of August in both years. In 2013, soil moisture content from the SPM was significantly higher than the LPM and CON. The soil moisture content of the FPP plot was significantly higher than the soil moisture content of the ANN plots. Soil temperature also followed a similar pattern as air temperature on the study site, with peak soil temperatures occurring in June and August in both years (Figure 2.2). The lowest soil temperatures were measured in October. There was no significant difference in soil temperatures between LPM and SPM in both years.

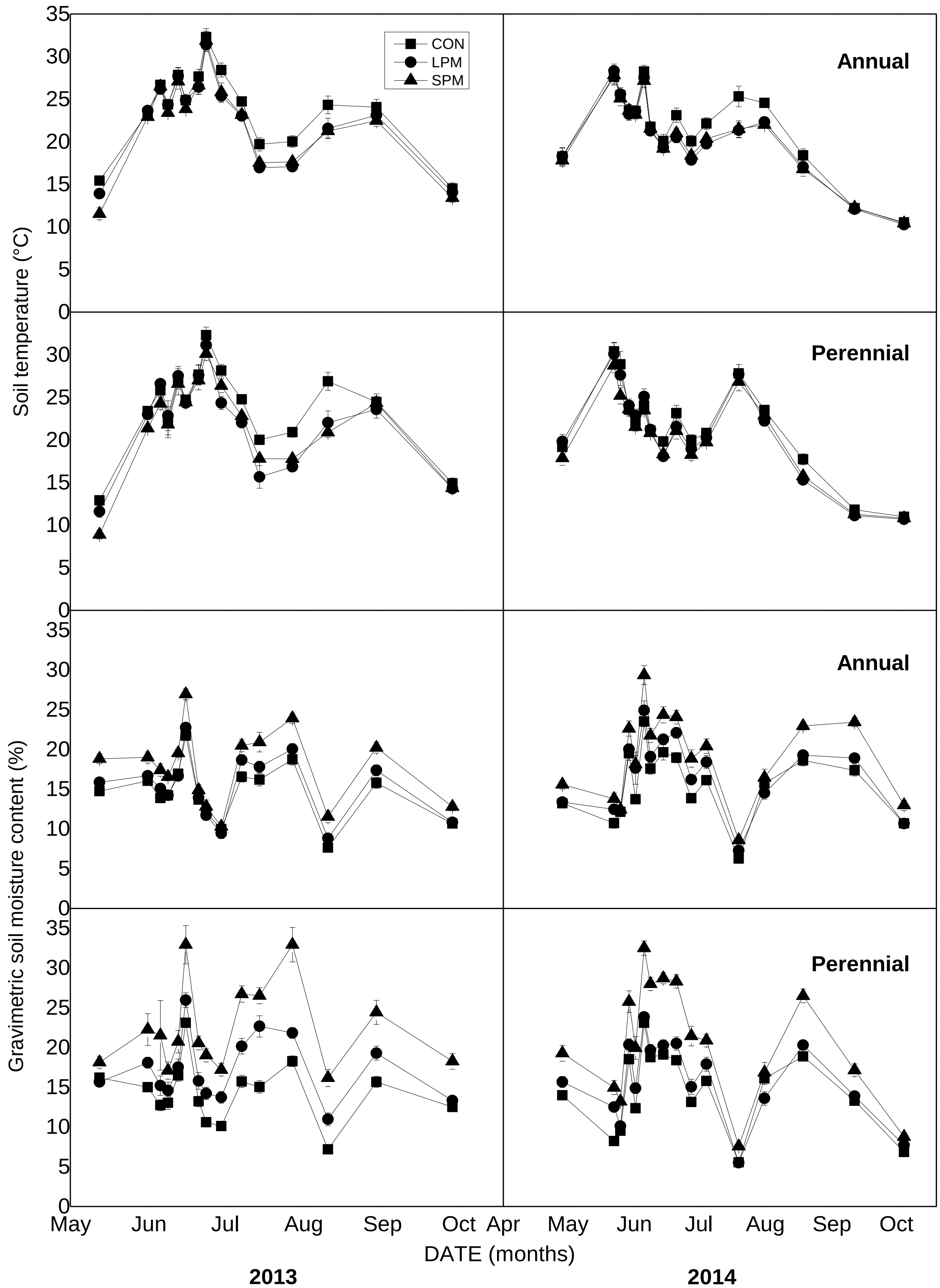


**Figure 2.2** Soil temperature at 0-2.5 cm (top) and gravimetric soil moisture content (bottom) in soil (0-10 cm) measured from the regular annual (ANN) plots and former perennial-perennial plots (FPP) amended with liquid (LPM) and solid (SPM) pig manures

### 2.4.4 Soil Ammonium Nitrogen

In 2013 and 2014, soil ammonium nitrogen from FPP was significantly greater than that of ANN ($p < 0.001$). There was no significant difference in soil ammonium nitrogen among the manure treatments. Ammonium nitrogen level was the greatest in the soil just after manure application, especially on LPM plots. As shown in Figure 2.3, on the first sampling date after the application of manure treatments, the ammonium content was the greatest in the LPM of the FPP plots in both years (138 ± 13 and 20 ± 8 mg N $kg^{-1}$ in 2013 and 2014, respectively) compared to LPM of the ANN plot (46 ± 11 and 7 ± 3 mg N $kg^{-1}$ in 2013 and 2014, respectively). As the season progressed, the ammonium nitrogen in the SPM plot became greater than that in the LPM.

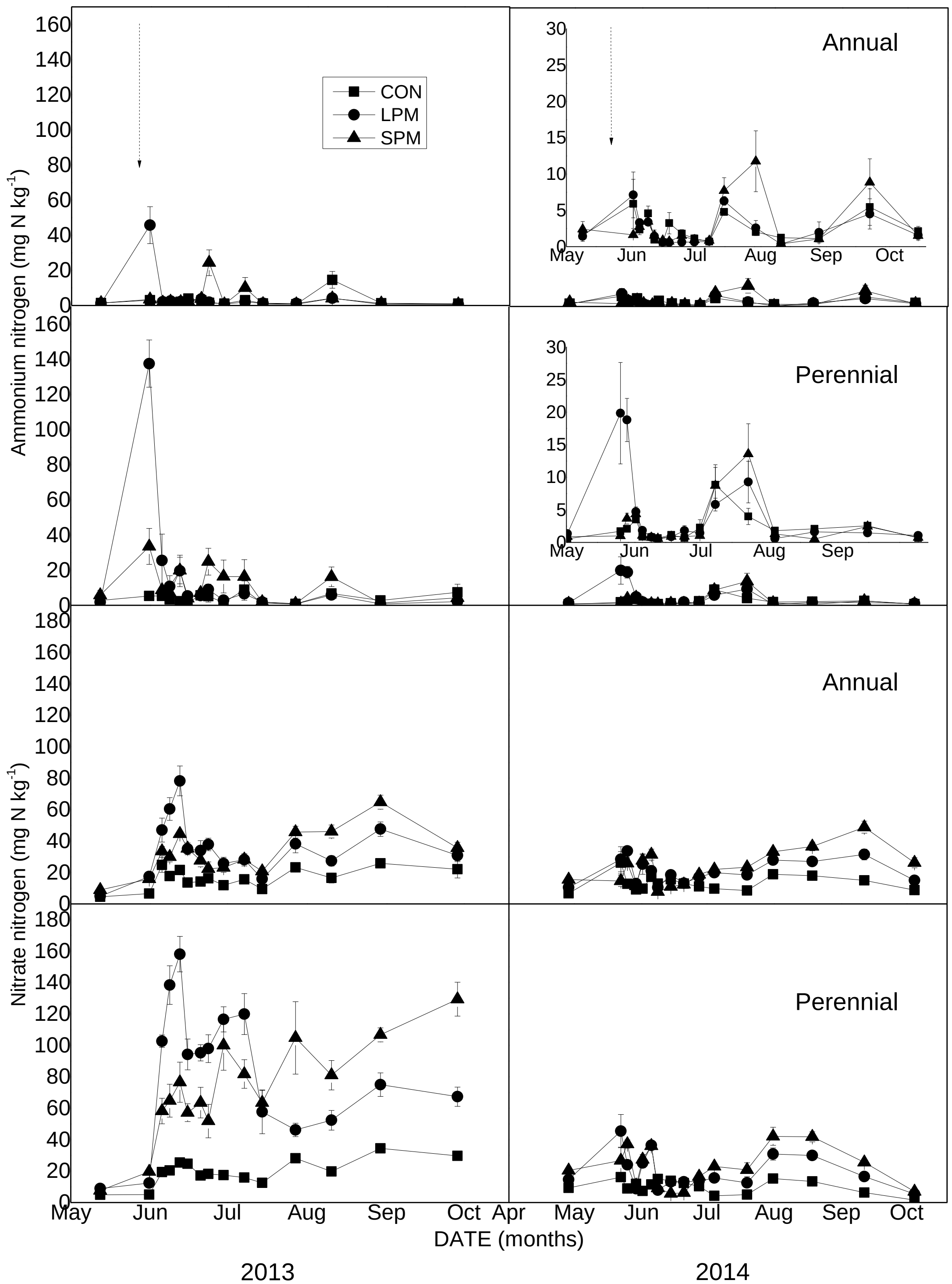


**Figure 2.3** Concentrations of ammonium nitrogen (top) and nitrate-nitrogen (bottom) in soil (0-10 cm) on the regular annual plots (ANN) and former perennial-perennial plots (FPP), amended with liquid (LPM) and solid (SPM) pig manures. Arrows indicate the date of manure application (11/June/2013 and 09/June/2014)

### 2.4.5 Soil Nitrate Nitrogen

Nitrate-N in soil from FPP was significantly higher than ANN in 2013 ($p < 0.001$) with a peak of 158 ± 11 mg N kg$^{-1}$ in the LPM treated FPP plots after two weeks of manure application compared to a peak of 78 ± 9 mg N kg$^{-1}$ in LPM treated ANN plot (Figure 2.3). At the end of the growing season in 2013, soil nitrate-N was far greater than the starting out soil nitrate-N in April by a factor of more than ten folds in the FPP (Figure 2.3). Except for FPP plots in 2014, before manure application in each year, nitrate-N was low and not statistically different among CON, LPM and SPM. In 2013, the year following perennial forage plow-down, average soil nitrate-N was significantly higher on FPP than ANN plots (Table 2.5). It is worth noting that more N was applied to the FPP in 2013 to meet its crop requirement (Table 2.2). Mean soil nitrate was higher on CON of FPP than CON of ANN, but crop yield was not significantly differenced between the two treatments in 2013. In 2014, when perennial forage grasses were replanted, average growing season soil nitrate-N was significantly higher in ANN than FPP plots. However, there was no significant difference in nitrate-N between LPM and SPM across the cropping systems. In 2014, a month after manure application (8$^{th}$ of July 2014), nitrate-N in the SPM treatment increased at a rate greater than that in the LPM treatment. As a result, the concentration of nitrate-N was high towards the end of the growing season with a peak of 49 ± 4 mg N kg$^{-1}$ of soil in the SPM treated ANN plots on the 29$^{th}$ September and 42 ± 3 mg N kg$^{-1}$ of soil on the FPP plots on the 5$^{th}$ of September. The average soil nitrate-N was higher in 2013 than in 2014.

**Table 2.4** Effect of manure treatments and cropping systems on cumulative $N_2O$ emission, emission intensity and emission factors.

| Year | Effect[a] | | Cumulative Emission | Emission Intensity[b] | | EF_Total N | EF_Total_Available N | EF_Target N |
|---|---|---|---|---|---|---|---|---|
| 2013 | Crop | | | | | | | |
| | ANN | | 0.83b | 0.20b | | 0.48b | 1.21b | 0.41b |
| | FPP | | 2.14a | 0.46a | | 0.73a | 1.79a | 1.62a |
| | Manure | | | | | | | |
| | CON | | 0.41b | 0.12b | | | | |
| | LPM | | 2.47a | 0.52a | | 0.88a | 1.82a | 1.30a |
| | SPM | | 1.57a | 0.34a | | 0.32b | 1.18a | 0.73b |
| 2014 | Crop | | | | | | | |
| | ANN | | 0.43a | 0.06a | | 0.37a | 0.78a | 0.25a |
| | FPP | | 0.29b | 0.02b | | 0.29a | 0.68a | 0.20a |
| | Manure | | | | | | | |
| | CON | | 0.14a | 0.03a | | | | |
| | LPM | | 0.41a | 0.05a | | 0.35a | 0.53a | 0.18a |
| | SPM | | 0.53a | 0.05a | | 0.31a | 0.92a | 0.27a |
| Model Effect | | df | Pr > F | | df | Pr > F | | |
| 2013 | Crop | 1 | <0.0001 | <0.0001 | 1 | 0.0283 | 0.0347 | <0.0001 |
| | Manure | 2 | 0.0021 | 0.0016 | 1 | 0.0174 | 0.1862 | 0.0491 |
| | Crop X Manure | 2 | <0.0001 | 0.0006 | 1 | 0.1334 | 0.2918 | 0.0757 |
| 2014 | Crop | 1 | 0.0396 | <0.0001 | 1 | 0.4028 | 0.6694 | 0.4959 |
| | Manure | 2 | 0.0642 | 0.3516 | 1 | 0.6617 | 0.2939 | 0.3847 |
| | Crop X Manure | 2 | 0.6990 | 0.3235 | 1 | 0.2124 | 0.4191 | 0.6221 |

**Note:** Least Square-means with the same letter in the same year under the same cropping system or manure treatments are not significantly different (Alpha=0.05).

[a]Cropping System, ANN = Regular Annual Plot, FPP = Forage Perennial Plots Manure Treatments, CON = unamended control, LPM =Liquid Pig Manure SPM = Solid Pig Manure

[b]In 2014, emission intensity was calculated using barley grain yield on ANN while forage biomass yield was used on FPP, as such figures are shown for observation purposes only and may not be suitable for actual comparison.

**Table 2.5** Cumulative $N_2O$ emission, soil available nitrogen levels, crop yield, emission intensity and $N_2O$ emission factors from the liquid (LPM) and solid (SPM) pig manure applied to the perennial (FPP) and annual (ANN) cropping systems.

| Year | Cropping System | Manure Treatments | Cumulative $N_2O$ | Mean Soil $NO_3^-$-N (2013, n = 180 2014, n = 192) | Mean Soil $NH_4^+$-N (2013, n = 180 2014, n = 192) | Crop Yield | Emission Intensity | EF_Total N | EF_Total_Available N | EF_Target N |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | (kg N ha$^{-1}$) | (mg N kg$^{-1}$) | | (Mg ha$^{-1}$) | (kg N Mg$^{-1}$) | (% kg N kg$^{-1}$ N applied) | | |
| 2013 | ANN (Canola) | LPM | 1.20bc | 35.22 ± 1.83b | 4.84 ± 1.07dc | 4.27ab | 0.30bc | 0.67b | 1.39a | 0.53bc |
| | | SPM | 0.85c | 32.15 ± 1.29b | 3.93 ± 0.76dc | 4.44ab | 0.19c | 0.28b | 1.03a | 0.29c |
| | | CON | 0.43c | 16.25 ± 0.75d | 2.68 ± 0.42d | 4.3ab | 0.10c | | | |
| | FPP (Canola) | LPM | 3.74a | 82.86 ± 3.74a | 15.72 ± 2.91ab | 5.04a | 0.74a | 1.09a | 2.26a | 2.06a |
| | | SPM | 2.29b | 71.10 ± 3.53a | 11.19 ± 1.54a | 4.46ab | 0.49b | 0.36b | 1.33a | 1.17b |
| | | CON | 0.39c | 19.54 ± 0.71c | 4.05 ± 0.54bc | 2.89b | 0.14c | | | |
| 2014 | ANN (Barley) | LPM | 0.52ab | 20.71 ± 0.95a | 2.32 ± 0.30b | 7.38 | 0.08a | 0.44a | 0.67a | 0.22a |
| | | SPM | 0.59a | 22.96 ± 1.01a | 2.99 ± 0.42ab | 8.69 | 0.07ab | 0.29a | 0.88a | 0.28a |
| | | CON | 0.18ab | 13.30 ± 0.62c | 2.47 ± 0.32ab | 4.08 | 0.05abc | | | |
| | FPP (Timothy + Orchard) | LPM | 0.31ab | 19.74 ± 1.15b | 4.50 ± 0.71a | 13.36 | 0.02bc | 0.26a | 0.38a | 0.15a |
| | | SPM | 0.47ab | 22.28 ± 1.20ab | 2.66 ± 0.42ab | 12.15 | 0.04abc | 0.33a | 0.97a | 0.26a |
| | | CON | 0.10b | 10.14 ± 0.37d | 2.15 ± 0.27ab | 8.53 | 0.01c | | | |

**Note:** Least square means with the same letter in the same year are not significantly different (Alpha = 0.05, Tukey-Kramer grouping). Values for available soil N are means ± SE**.**

## 2.5 Discussion

### 2.5.1 Effect of Converting Perennial Forage Grass System to Annual System On $N_2O$ Emissions

Perennial forage plow down resulted in more available nitrogen and $N_2O$ flux from the plots with continuous application of manure but not on the control plots (Figure 2.3). In 2013, the average soil nitrate-N and ammonium-N were significantly higher on FPP than ANN (Figure 2.3). The values of soil nitrogen from manured FPP in 2013 from this study far exceeded those of previous manured studies on this site by 250 % (Karimi et al. 2017; Nikièma et al. 2016). The mineralization of N from residues of the terminated perennial forage grasses would have contributed to increased nitrate content in the soil. This is in agreement with the work of Chantigny et al. (2013), who reported an increase in soil nitrogen content following termination of manured forage grasses and observed that it served as a source of nutrient for the crop grown on the same plot in the following season. Perennial forage grasses are known to store large amounts of nitrogen and carbon (Bolinder et al. 2002). Since the FPP plots have been in the grass phase for four years with continuous application of manure before cultivation occurred, this system must have accumulated a significant amount of organic C and N in the soil (Bolinder et al. 2012). This organic input could have been markedly affected by the cultivation that occurred in the fall of 2012 and spring of 2013. Cultivation would have increased the rate of decomposition of the organic material, thus providing the necessary substrate for nitrification and denitrification processes in soil. Another factor that could have contributed to the increased N level in the soil is the amount of manure applied to the FPP plots in 2013 to increase the historically low residual N content in the soil and meet the N requirement for the crop. The applied manure N to the FPP plots was more than 250% that of ANN. This rate difference of total N and total available N likely explains the amount of $NO_3^-$-N released in the soil during the growing season of the year 2013. The N difference did not result in significant yield difference probably because there was a larger quantity of available N in soil than the ability of the crop to uptake it.

The increased $N_2O$ emission following the termination of perennial forage grasses is consistent with results from other studies (Drewer et al. 2016; Mielenz et al. 2017). Fraser and Amiro (2013) also pointed out a deficit in carbon balance following the conversion of manured perennial forage to annual cropland. Nitrification and denitrification are principal processes contributing to $N_2O$ emission from the terminated perennial forages grasses, as explained by Snyder et al. (2009) and Wrage et al. (2004). Soil $O_2$, $NO_3^-$-N, and C are proximal regulators of nitrification and denitrification processes in the soil, which are, in turn, affected by distal factors such as environmental conditions on the field (Barton et al. 1999; Wallenstein et al. 2006; Sahrawat 2008). Lasisi et al. (2017) reported that FPP was able to keep the manure applied N in $NH_4^+$-N form which reduced the risk of it being lost through leaching (Karimi et al. 2017). Nikiema et al. (2012) also found soil nitrification potential to be seven-times higher in a recently cultivated pasture hayfield than that of an uncultivated reference pasture site. The increased supply of available N from N mineralization of both SOM and the plow-down perennial forage grasses, coupled with the continuous application of manure to the plots, was likely responsible for the elevated $N_2O$ emission following the conversion of the perennial forage crops to annual crops (Drewer et al. 2016). The ANN and FPP systems received similar manure treatments annually based on crop requirement and residual soil nitrate in the soil, although more N was added to FPP in 2013 to increase the low residual N level in the soil in order to meet crop requirement. The elevated soil available N level and $N_2O$ emissions in FPP relative to the ANN, must be the results of accelerated N mineralization from these organic inputs that were greater in the FPP than in the

ANN system. The emission of $N_2O$ was not significantly different between the CON treatment of the FPP and that of the ANN, which might also suggest that the observed difference between the manure treated plots was due to manure addition to the plots rather than crop residues incorporation.

2.5.2 Effect of grass system re-establishment on $N_2O$

In 2014, the average $NO_3^-$-N content in soil was within the range reported in previous manured studies at this site, ranging from a low of 4 mg N $kg^{-1}$ of soil on the control plots to a high of 30 mg N $kg^{-1}$ on treated soils (Karimi et al. 2017; Nikièma et al. 2016). When the system returned to grassland in 2014, available N and $N_2O$ fluxes were smaller in the FPP than in the ANN system, suggesting that the accelerated N mineralization from the previous organic inputs had significantly slowed down and/or the FPP system has become more efficient at utilizing any soil available N inputs from SOM mineralization and manure addition than the ANN system.

In 2014, when the perennial forage grasses were re-established, cumulative $N_2O$ flux, emission factor and emission intensity were lower on FPP compared to ANN. This agrees with the report of Mass et al. (2013) who observed that $N_2O$ flux from ANN quadrupled that of FPP. On the contrary, Nikièma et al. (2016) observed inconsistency in $N_2O$ flux between ANN and FPP. Oates et al. (2016) reported a 142% increase in $N_2O$ flux from annual crops over perennial grasses. They concluded that perennial crops emit less $N_2O$ during their establishment phase compared to annual crops.

### 2.5.3 Effect of Manure Type

For the entire growing season, there was no statistical difference between $N_2O$ flux from LPM and SPM. However, in both years, following manure applications, available soil N was higher on LPM compared to SPM (Figure 2.3). There are various characteristics of LPM that can facilitate quick release of N and optimize $N_2O$ emission from LPM compared to SPM. These include i) greater $NH_4^+$-N content, ii) greater soil moisture content, and iii) greater amounts of soluble organic carbon (Chadwick et al. 2011). The LPM has most of its N content in the $NH_4^+$ form (Table 2.1), which is a readily available N form in the soil soon after manure application. The high $NH_4^+$-N concentration in the liquid pig manure (Table 2.1) must have stimulated the size and activities of soil nitrifying bacteria communities, which in turn quickly nitrified the $NH_4^+$ to $NO_3^-$- N and the subsequent release of $N_2O$ in the process. This was evidenced by the soil $NH_4^{+-}$N and $NO_3^-$-N concentrations from the LPM plots, which appeared to be the highest during the first few weeks of manure application, both in 2013 and 2014 (Figure 2.3). This could also be observed from the $N_2O$ flux data. About one to two weeks after manure application, the $N_2O$ flux from LPM was three times greater than that of SPM (Figure 2.1). The only exception to this was ANN treatments in 2014, although, the $NH_4^+$ in SPM of 2014 was comparatively high (Table 2.1).

Additionally, LPM is made up of more than 93% water compared to 75% for SPM (Table 2.1). Application of LPM may increase soil water content and likely create conditions that promote the decomposition of soil organic materials. Although this moisture increase may be momentary, it can serve to initiate other processes in the soil.

Thirdly, the amount and type of organic C compounds available for microbial decomposition in manure could also potentially influence the rate of decomposition of organic materials. LPM has the majority of its C in a soluble form, unlike SPM that has its C embedded in a straw matrix, and is less available for microbial decomposition (Chadwick et al. 2011; Nikièma et al. 2016; Rochette et al. 2008). As seen in Table 2.2, SPM has higher C:N ratios compared to LPM (Eiland et al. 2001; Qian and Schoenau 2002). Thus, it takes longer time for soil microbes to decompose organic C of SPM compared to that of LPM. Due to this slower decomposition process, nitrification and denitrification rates and their subsequent release of $N_2O$ may also be reduced from the SPM amended soil. Another consideration is the oxygen consumption under LPM, which may be high compared to SPM, thus leading to an increased likelihood of anaerobic microsites that tend to promote denitrification and increased $N_2O$ flux.

### 2.5.4 Effect of Environmental Factors

In this study, soil moisture showed a strong relationship with $N_2O$ fluxes (Table 2.6). This is in support of previous work on soil moisture and the $N_2O$ flux relationship (Nikièma et al. 2016). Soil moisture explained up to 30% of the variations in $N_2O$ fluxes on most of the treatments. The strong correlation of soil moisture with $N_2O$ flux is an indication that denitrification is one of the dominant processes controlling $N_2O$ flux on this site. Early in the growing season, around June, soil moisture was high, with water-filled pore space values being greater than 60 %. This coincided with the high $N_2O$ flux periods after manure application each year. Tenuta et al. (2010) reported the most robust relation with $NO_3^-$-N while they observed a negative relationship between soil moisture and $N_2O$ flux. They suggested that the negative correlation may be because the nitrification process was inhibited at higher soil moisture or the denitrification process went to completion with $N_2O$ being converted to $N_2$.

Soil moisture and temperature are important environmental factors that affect $N_2O$ fluxes in agricultural fields. Soil moisture controls the availability of oxygen in the soil. At high moisture content, oxygen is limited. Thus $NO_3^-$ can be used as an electron acceptor by denitrifying organisms. The significantly higher moisture in SPM than LPM may be attributed to improved water holding capacity of the soil because of reduced bulk density from organic materials in the soil (Adesanya et al. 2016). Also, SPM acts like mulch protecting the soil, improving water infiltration and loss through evaporation.

Soil temperature did not differ significantly between SPM and LPM treatments but was lower than the CON (Figure 2.1). Plots amended with manure likely produced more biomass (improved crop growth) and maintained more vegetative or biomass groundcover than the control ones except in 2013. An increase in temperature is believed to increase microbial activities which may aid nitrification and denitrification processes; this effect may sometime be masked by other factors such as management practices. Soil temperature equally had a strong relationship with $N_2O$ flux from this study (Table 2.6). Early in the growing season, around June and July, $N_2O$ fluxes were high following manure application. Note that this period of elevated $N_2O$ fluxes also coincided with a warmer period when soil temperatures ranged between 20 and 30 °C. This range of temperature is known to stimulate soil microbial activity. Whereas, in October, when soil temperature was low, most especially in 2014, when soil temperature was below 10 °C, biological activities might have been equally reduced and $N_2O$ flux was at a minimum.

**Table 2.6** Pearson's correlation coefficient and level of significance between normally transformed daily nitrous oxide flux and measured soil variables across the two years. The cropping treatments are annual plots (ANN) and former perennial plots (FPP), while the manure treatments are liquid pig manure (LPM), solid pig manure (SPM) and control (CON). n <= 367

| Cropping System | Manure Treatments | $N_2O$-N correlation coefficients | | |
|---|---|---|---|---|
| | | Soil Temperature | Soil Moisture | Soil Available N |
| ANN | LPM | 0.32 *** | 0.26 *** | 0.24 *** |
| | SPM | 0.37 *** | 0.26 *** | 0.02 ns |
| | CON | 0.26 *** | 0.33*** | 0.14 * |
| FPP | LPM | 0.28 *** | 0.27 *** | 0.60 *** |
| | SPM | 0.25 *** | 0.21 *** | 0.37 *** |
| | CON | 0.23 *** | 0.17 ** | 0.22 ** |

**Note:** ns not significant, * significant (P < 0.05), ** very significant (P < 0.01), *** highly significant (P < 0.001).

## 2.6 Conclusion

During the perennial forage crop phase (2014), the annual system emitted more $N_2O$ than the perennial system, suggesting some $N_2O$ savings from the perennial relative to the annual system. It can be therefore be recommended that including a perennial forage crop in rotation with an annual crop system is a good strategy to reduce $N_2O$ emission from the whole system. However, when the perennial system was converted to an annual system, the disturbed soil emitted significantly more $N_2O$ than the regular annual system, suggesting more $N_2O$ loss from the cultivated grassland soil. Cumulative $N_2O$ emission and emission intensity were not significantly different between the control plots of ANN and FPP plot, which may be an indication that the manure applications in conjunction with cropping systems were the driving factor for the emissions observed. This result also suggests that a great deal of the N accumulated during the forage grass phase when manure N was continually applied could be lost during the year of land use conversion alone, thus reducing the overall GHG benefits. I do know that the $N_2O$ emission was high during the first growing season following the perennial grass cultivation. However, since the FPP plots were reseeded to forage grasses during the next growing season, I do not know how significant the $N_2O$ flux would have been that year (2014) if the plots were still used for annual crops. Further investigations are therefore needed to determine the $N_2O$ implication and the best crop rotation time (time of grass phase vs. Time of annual phase) that would provide the maximum GHG, particularly $N_2O$ benefit.

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# 3. NITROUS OXIDE FLUXES FROM LIQUID PIG MANURE AND UREA FERTILIZER APPLIED TO ANNUAL CROP

## 3.1 Abstract

Manure can serve as a comparable source of nitrogen (N) as synthetic fertilizer; however, soil nitrous oxide ($N_2O$) fluxes may differ substantially between these two N sources. This study was carried out during three growing seasons (2011, 2013, and 2014) in an agricultural field plot with a sandy loam soil, cropped to either barley (*Hordeum vulgare* L.) or wheat (*Triticum aestivum* L.). The experiment included three treatments in a randomized complete block design with four replicates: zero N amendment (CON), liquid pig manure (LPM) at a rate of 56,000 L $ha^{-1}$ $yr^{-1}$, and urea (FER) at N rate matching the total available N content in the manure. In all three years, crop yield and N uptake was slightly higher in the LPM treatment compared to the FER treatment, but the difference was not statistically significant. In 2011 and 2014 when applied N rate was moderate but the application time coincided with a long period of drought, cumulative $N_2O$ emissions, emission intensity and factor were significantly higher in the FER treatment than in LPM treatment. In 2013, however, when applied manure N was relatively high, and soil moisture mostly adequate, no such effect was observed. Soil available N content, temperature, and moisture were positively correlated ($P < 0.05$) with $N_2O$ emission in both LPM and FER samples, and explained about 40% of the overall variability of $N_2O$ emission. We conclude that the use of liquid manure N in cropping system is an environmentally advisable strategy. However, from both nutrient management planning and $N_2O$ emission reduction stand points, the results of this study highlight the challenges associated with manure N variability, and emphasis the need for applying manure based on its known N content so that application rate can meet the crop N demand and minimize $N_2O$ emissions.

### 3.2 Introduction

With an increasing world population, there is a need to increase food production sustainably while conserving the environment. Intensive agriculture coupled with increased used of nitrogen (N) fertilizers has significantly contributed to elevated atmospheric greenhouse gases (GHGs) known to cause global warming and climate change (IPCC 2014). The agricultural sector is the main contributor to nitrous oxide ($N_2O$) emissions, mainly from manure and fertilizer management (Environment Canada 2014; Mosier et al. 1998). $N_2O$ is a powerful greenhouse gas (GHG) with a global warming potential of 265 times greater than that of carbon dioxide ($CO_2$) over a hundred years period (Myhre et al. 2013). Nitrogen present in, or added (as manure or synthetic fertilizers) to soil is subject to several changes or transformations, which dictate its availability to plants and potential losses to the environment through either gaseous emission (i.e. ammonia ($NH_3$), $N_2O$, and $N_2$) or leaching of nitrate ($NO_3^-$). In soils, $N_2O$ is produced during nitrification and denitrification processes driven by soil nitrifiers and denitrifiers (Khalil et al. 2004; Kool et al. 2011). Temperature and moisture are important environmental factors that influence the activity of soil nitrifiers and denitrifiers and, therefore, the mineralization, oxidation or reduction rates of soil N.

Liquid pig manure (LPM) is waste effluent from pig farms containing mainly animal faeces, urine and wash water. It is rich in essential plant nutrients, and high in $NH_4$ compared to other sources where most N is in organic form, making it a close substitute for other sources of N for plants such as urea fertilizer. As of 2019, there were over 769 million heads of pig in the world, of which 21 million were produced in Canada. A pig can generate five liters of liquid pig manure every day. The storage and safe disposal of this large volume of manure produced by pigs can become challenging. Agricultural land application is a traditional way to recycle the pig manure.

For better nutrient management, farmers are advised to conduct a soil test of their farm and manure nutrient analysis to determine the optimal manure rate before applying it to the field. However, obtaining laboratory analysis results of manure prior to application is often challenging for most farmers. This is because manure storage structures are not generally agitated until just before and during pump-out. Consequently, the use of literature mean nutrient values of manure has become a common practice in some regions, including Manitoba. However, due to several factors such as differences in diets, bedding, amount of water entering the storage facility, degree of agitation, manure nutrient contents from individual farms may vary significant and sometime be different from literature reported average values (Hatfield et al. 1993; Saggar et al. 2004).

Although $N_2O$ emissions associated with manure and synthetic N fertilizer applications to agricultural lands have been investigated for several decades, only few studies have compared soil $N_2O$ emissions from liquid pig manure and urea fertilizer applied to annual cropland in the Canadian prairie. Nikièma et al. (2016) examined the application of liquid pig manure (LPM) and solid pig manure (SPM) to annual grains (barley and canola) and perennial forages (timothy and orchard grasses) crops on a sandy loam soil in Manitoba. They observed that environmental conditions such as moisture and temperature were the major factors contributing to variation in $N_2O$ fluxes. Also, Gao et al. (2014) examined the effect of adding pig slurry to a sandy loam soil in Southern Manitoba, on $N_2O$ release and they reported that $N_2O$ fluxes increased with increase in rate of pig slurry N application. Mkhabela et al. (2008) indicated that potassium nitrate had more cumulative $N_2O$ emission compared with pig slurry and ammonium sulfate, showing that nitrate provides the direct substrate needed for $N_2O$ emission. Asgedom et al. (2014) observed that pig manure induced lower $N_2O$ emissions than urea fertilizer when applied to rapeseed and spring wheat on clay soil in Manitoba. Although rapeseed and wheat yield from the treatments receiving pig manure application was less than plots that received urea, which was attributed to reduced N supply. On the other hand, Clayton et al. (1997) observed that manure has the highest $N_2O$ emission compared to other inorganic fertilizers such as urea, ammonium nitrate, calcium nitrate and ammonium sulfate. Similarly, Petersen (1999) observed the highest $N_2O$ emissions from untreated manure slurry compare to urea fertilizers.

The fraction of N from the fertilizer that is lost as $N_2O$ may vary not only with environmental factors (e.g., climate, soil conditions, etc.) but also with fertilizer type. Organic and inorganic fertilizers, due to their composition and interactions with environmental factors, may impact nitrification and denitrification in soil differently. For instance, available C in manure is an excellent substrate for microbial activity (including denitrification). One may hypothesize that the addition of organic amendments such as LPM at a constant rate annually will result in higher $N_2O$ emission than synthetic N fertilizer sources (urea). The objective of this study was to estimate and compare crop yield and N uptake as well as growing season daily and cumulative $N_2O$ fluxes from liquid pig manure and urea fertilizer applied to annual cereal crops.

## 3.3 Materials and Methods

### 3.3.1 Site Description

This study was conducted on a commercial annual grain farm in the Rural Municipality of North Cypress, Carberry, Manitoba, Canada (lat. 49° 55.950'N, long. 99° 31.288'W, elevation 383.5 m). Carberry is in a cold subhumid temperate region with an annual average soil temperature of 2.1 °C and average annual precipitation of about 528 mm, the majority of which falls as rain from April to October. The vegetation in the region is dominated by oak, shrubs, and prairie grasses. The soil type on the site has been mapped as moderately well-drained loamy fine sand, Fairland soil series, an Orthic Black Chernozem under the Canadian System of Soil Classification (Ehrlich et al. 1957; Haluschak and Podolsky 1999). The soil has a bulk density of 1.3 g $cm^{-3}$ and pH of 6.4 at the soil surface (Vivekananthan 2014).

### 3.3.2 Experimental Layout and Agronomic Treatments

This study was carried out during the growing season (April – October) of 2011 to 2014 on a long-term experimental plot at Carberry. In 2012, a lower rate of N was inadvertently applied to the FER (Urea fertilizer plots) than the LPM plots, and as such, the results obtained in 2012 were excluded from the analysis here but made available in the supplementary section. The history of this study site, which started back in 2002, has been described by Nikièma et al. (2013) and Karimi and Akinremi (2018). Liquid pig manure (LPM) was applied at a rate of 56,000 L $ha^{-1}$ $yr^{-1}$. This volume was determined based on farmer practices and literature values of N content in liquid manure from commercial pig barn in Manitoba. The actual liquid manure N application rates were back-calculated using manure nutrient analysis results from samples collected before manure application time. A similar N rate of urea fertilizer was applied to FER plots to match the N rate of LPM plots. The plots were seeded to either barley (*Hordeum vulgare L.)* or spring wheat

(*Triticum aestivum* L.), spring wheat at the start in 2011, spring wheat in 2012, barley in 2013 and spring wheat again in 2014. The experimental design was a randomized complete block design with three treatments and four replicates.

The liquid pig manure was obtained from a manure lagoon on a pig farm in Manitoba, Canada and analyzed for N content to determine the equivalent amount of urea fertilizer to be applied to the FER plots (Table 3.1). According to the Prairie Province's Committee on Livestock Development and Manure Management (2004), it is estimated that 25% of liquid pig manure ammonium nitrogen is lost through volatilization when manure is applied and incorporated on the same day and that only 25% of the organic nitrogen is available to crop during the first year of its application. The LPM was metered out in 10 L-jugs broadcasted on the plots and incorporated immediately by tillage, usually within 2 hours of the start of the application process. This follows general practice in this region to incorporate manure or fertilizer after application into the soil to reduce ammonia volatilization losses. Urea fertilizers were equally broadcasted manually by hand to the FER plots based on calculated values and incorporated within 2 hours (Table 3.1).

All plots were cultivated using a tandem disc plow, incorporating manure and fertilizer treatments to a depth of 10 cm. The same treatment was applied to the same plot each year of the study. Treatment application dates from 2011 to 2014 were 26$^{th}$ June 2011, 23$^{rd}$ May 2012, 17$^{th}$ June 2013, and 11$^{th}$ June 2014, respectively. Using an air-seeder, in 2013, barley (*Hordeum vulgare* L. variety Tradition*)* was seeded at a rate of 125 kg ha$^{-1}$ while in 2011 and 2014, wheat (*Triticum aestivum* L. variety Brandon) was seeded at a rate of 100 kg ha$^{-1}$. Seeding was usually done on the same day as manure and urea application and incorporation. Agronomic management included herbicide application at 4-week growth stage using a mixture of Curtail$^{TM}$ M (clopyralid 50 g a.e./L + MCPA 280 g a.e. l$^{-1}$) and Puma 120 (Fenoxaprop-P-ethyl/Mefenpyr-diethyl 120:33

g $l^{-1}$) applied at a rate of 2 L $ha^{-1}$ and 0.6 l $ha^{-1}$, respectively, for broadleaf weed and annual grass control.

**Table 3.1** Manure dry matter and nitrogen content and application rates of nitrogen from the liquid pig manure (LPM) and urea fertilizer (FER) applied to the plot in 2011, 2013 and 2014.

| | Manure Dry Matter and N Content | | | N Application Rates | | | |
|---|---|---|---|---|---|---|---|
| **Year** | **Dry matter** (kg kg$^{-1}$) | **Total N** (mg L$^{-1}$) | **$NH_4^+$-N** (mg L$^{-1}$) | **Volume of LPM** (L ha$^{-1}$) | **Total Manure N Applied** (kg N ha$^{-1}$) | **LPM Total Available N Applied** (kg N ha$^{-1}$) | **FER Urea N Applied** (kg N ha$^{-1}$) |
| 2011 | 0.022 | 1650 | 1357 | 56,000 | 92 | 80 | 80 |
| 2013 | 0.070 | 4874 | 2710 | 56,000 | 271 | 180 | 180 |
| 2014 | 0.014 | 1637 | 1351 | 56,000 | 91 | 80 | 80 |

Note: Total available N applied is the amount of N expected to be available in the soil for plant use within a year, this is calculated as

$$Total\ Available\ N = \mathrm{NH_4^+}\text{-N} \times (100\ \% - 25\ \%\ \mathrm{NH_4^+}\text{-}N\ volatilization\ loss) + 25\ \%\ Organic\ N$$

### 3.3.3 Gas Sampling

Gas samples were taken on 15 dates during the growing season each year from April to October. One sample was taken a day or two before the manure/fertilizer application date. Following manure and urea applications, two samples were collected per week during the first three-week period when I expected $N_2O$ emissions to be most vigorous. Sampling intensity was reduced to one sample per week from week 4 to week 8, once fortnightly for week 9 to 12, and finally reduced to one sample a month for the rest of the growing season. This sampling intensity was determined based on previous greenhouse gas emission measurement studies conducted on plots with a similar soil in this area (Nikièma et al. 2016; Tenuta et al. 2010).

The closed static vented chamber technique was used for the collection of the gas. Three polyvinyl chloride (PVC) round collars of 20.3 cm internal diameter and 15 cm height were deployed in each plot. The bottom edge of the chamber was beveled to facilitate driving into the soil. Four 5 cm tack-screws were attached to the exterior of the chamber to hold the rubber bands used to secure the lid. The lids for the chambers were constructed from a similar material, a flat PVC material cut to the circular pattern of radius 11 cm. One side of the lid was covered with aluminum foil, the side facing up. The lid contained a rubber septum (1.45 cm outer diameter) and an air vent 4.5 mm internal diameter and 9 cm long. A rubber gasket made from bicycle tire tubing was used to cover edges of the lids and the gas chambers to avoid gas loss from the chamber (Nikièma et al. 2016).

Three collars were randomly deployed in each plot, at least 2 m apart and inserted 5 cm deep into the soil. Unless when there was major field management operations such as herbicide application or harvesting, gas collars were left permanently on the field uncovered. In this way plants were able to grow in the collar undisturbed while this minimized disturbance to the soil during gas sampling. However, when plant posed a hindrance to the closure of collar during sampling, they were trimmed to sizes, 5 cm above ground level. On each gas sampling occasion, four gas samples were collected from each chamber within 45 minutes following lid placement. Using a 20 mL polypropylene syringe (Becton-Dickinson, Franklin Lakes, NJ), gas was withdrawn from the chamber headspace into the syringe. The first pull of the plunger was used for flushing the syringe, while 20 mL of gas was withdrawn with the second pull of the plunger, and transferred into a pre-evacuated 12 mL Exertainer vial (Labco Exetainer, High Wycombe, UK) fitted with butyl rubber septum. The time of each gas sampling was recorded. The processes were repeated every 15 minutes. Samples were stored in a cool dark environment until analysed in the laboratory. At the end of the fourth round of gas sampling, the lids were removed. The height of the chambers above the ground level were measured from four different locations inside the collar and used to calculate the headspace volume of the gas chambers.  For quality assurance and control, high and low reference $N_2O$ and pure $N_2$ gas samples from the laboratory were taken to the field each time and subjected to the same conditions as samples. Measurements were usually taken in the morning from 10:00 am – 12:00 noon on each sampling day. The temperature at this period is representative of the daily average thus allowing upscaling of our result to daily values. Soil and ambient air temperature at the time of sampling were also taken before chamber closure. The gas samples in the vials were taken to the laboratory and analyzed for $N_2O$ using a Varian GP 3800 gas chromatography analyzer (Varian Canada, Mississauga, ON) fitted with an electron capture detector (ECD) for detection of the gases. After each use, vials were evacuated by repeated suction method using Thermo Scientific™ Direct-Drive vacuum pump (Model: P-420, Thermo Fisher Scientific Inc., MA, USA) and flushing with helium gas. Calibration standards were prepared by dilution of a known $N_2O$ concentration standard (Praxair Canada Inc, Mississauga, ON), which was used in determining the concentration of the unknown samples. Blank samples and standardized reference samples from the field were placed at start and every interval of 25 samples. When reference samples deviated from expected values by more than 5%, the machine was checked for error sources and corrected as necessary while the whole sample batch was reprocessed.

The flux rates were calculated as a function of chamber headspace concentration against time, using the HMR procedure, an improved Hutchinson and Mosier (1981) method as reported by Pedersen et al. (2010). This procedure is made available as an HMR package, a free add-on in R programing software (available at https://CRAN.R-project.org/package=HMR). Based on the concentration gradient of trace-gases, the procedure recommends the best of three choices for calculating the flux and presents the user with a graphical interface, 1. Non-linear exponential curve (HMR), 2. The linear model (LR), 3. No flux, which may indicate flux below the detection limit or resulting from experimental error. In most cases, I accepted the recommendation of the HMR package, majority of which followed LR trends, except in no flux when I observed the graph to see if it fits LR. The resulting $N_2O$ flux data were scaled to g N $ha^{-1}$ $d^{-1}$. Linear interpolation was employed as the method of gap filling for days in which samples were not taken. Cumulative growing season $N_2O$ emissions were calculated for each chamber by summing up daily interpolated flux from the start of sample collection (May) to end of sample collection (October) each year.

### 3.3.4 $N_2O$ Emission Factor, Emission Intensity and Crop Yield Estimation

At the end of each growing season, crops were harvested mechanically by cutting just above ground level. Crop yield was estimated using a 0.25 $m^2$ quadrat measuring 50 cm by 50 cm. Four harvest locations were randomly selected within each plot for harvest while maintaining three rows within each quadrant. The four samples were bulked together in a jute bag making a total area of 1 $m^2$; this was dried inside a well-ventilated drying room at a temperature of 35°C for 30 days. Grain was separated from the rest of the plant material by threshing. The calculation step is as described below.

The $N_2O$ emission factor and emission intensity were calculated using;

$$\text{EF\_Total\_N} = \left(\frac{\sum(\text{N}_2\text{O-N})\ \text{Amended soil} - \sum(\text{N}_2\text{O-N})\ \text{Control}}{\text{Applied Total N}}\right) \times 100 \quad \text{-------------------- (1)}$$

$$\text{EF\_Total\_Available\_N} = \left(\frac{\sum(\text{N}_2\text{O-N})\ \text{Amended soil} - \sum(\text{N}_2\text{O-N})\ \text{Control}}{\text{Applied Total Available N}}\right) \times 100 \quad \text{-------------------- (2)}$$

Where EF_Total_N = $N_2O$ emission factor calculated based on total nitrogen applied

EF_Total_Available_N = $N_2O$ emission factor calculated based on total available nitrogen applied

$\sum(\text{N}_2\text{O} - \text{N})$ Amended soil = Cumulative $N_2O$–N from the amended plots (kg N $ha^{-1}$). $\sum(\text{N}_2\text{O} - \text{N})$Control = Cumulative $N_2O$-N from the control plots (kg N $ha^{-1}$)

Applied total N = total nitrogen in the manure or fertilizer that was applied to the amended plots (kg N $ha^{-1}$).

Applied total available N = Available nitrogen in the manure less 25% loss due to volatilization plus 25% of organic N that will be mineralized during the growing season (kg N $ha^{-1}$).

Note: No volatilization losses were assumed for urea.

$$\text{Emission intensity} = \frac{\sum(\text{N}_2\text{O} - \text{N})}{\text{Grain yield}} \quad \text{------------------------------------------------------------- (4)}$$

*Where* $\sum (N_2O\text{-}N)$ = cumulative $N_2O$-N from the treatment (kg N $ha^{-1}$), Grain yield = average grain yield of wheat or barley from the treatment (Mg $ha^{-1}$)

### 3.3.5 Soil Sampling and Ancillary Measurements

Soil samples were collected near each gas chamber from a depth of 0 to 10 cm using a Dutch auger of 4 cm inner diameter (Soil Moisture Equipment Corp., CA). On each sampling occasion, as earlier described under gas sampling, soil samples were taken from two locations randomly selected near each gas chamber, bulked into a bag and kept in the dark, cool, dry place while in the field. Samples were then taken to the lab where they were refrigerated at 4 °C and analyzed within a week for gravimetric soil moisture, extractable ammonium-nitrogen ($NH_4$-N), and nitrate-nitrogen ($NO_3$-N) contents. Soil samples were analyzed for $NH_4$-N and $NO_3$-N using an AQ2 AutoAnalyser (SEAL Analytical Inc., WI) fitted with a spectrophotometer. The soil moisture content was determined gravimetrically using the oven-dry method at 105 °C for 24 hours. Soil temperature near the gas chambers on the field was measured during each sampling period to a depth of 2.5 cm using a Fischerbrand traceable digital soil thermometer, CAT. 15-077-59 (Thermo Fisher Scientific Inc., MA). Weather data containing air temperature and precipitation were obtained from weather station placed at the center; this was used in conjunction with Agriculture and Agri-Food Canada weather station, located 5 km from the study site.

### 3.3.6 Statistical Analysis

The GLIMIX procedure in SAS® software (Schabenberger 2005) was used to analyze the data for differences in treatments. The UNIVARIATE procedure was used to test the data and residuals for the assumption of normality. Log-normal data distribution was used for the following variables $NO_3^-$-N, $NH_4^+$-N, and $N_2O$ fluxes, as the data did not conform to the test of normality according to Shapiro–Wilk's test. A repeated-measures analysis of variance was performed. The fixed effects were treatment (LPM, FER and CON) and sample date, while year and block (replicate) were random factors. The three collars in each plot were nested within treatments and blocks. Cumulative $N_2O$, emission factor, emission intensity and grain yield were analysed as randomized complete block design (RCBD) with the treatments (LPM, FER and CON) being fixed effect. Means were separated using Tukey-Kramer adjustment at an alpha level of significance of 0.05. Pearson's correlation and multiple linear regression analysis were used to assess the relationship between soil nitrogen, soil temperature, soil moisture and natural log-transformed $N_2O$ flux.

## 3.4 Results

### 3.4.1 Environmental Condition

In Manitoba region, most of the rain falls between April and October, which is the growing season in which this study was carried out. The year 2011 was very dry, with annual precipitation of 275 mm in comparison with the long-term normal of 530 mm (Table 3.2). The previous year 2010 was wet in the region with annual precipitation of 528 mm. 2013 was moderately wet during the growing season. June of 2014 was wetter than normal, which coincide with when manure and urea fertilizer treatments were applied. This was followed by a dry spell in July of the same year, which was evident in the soil moisture data (Figure 3.1) as the soil moisture was close to saturation in June and then gradually declined below 7 % gravimetric moisture content in July of the same year. The months of July and August are the warmest month of the year in the study area, with a mean monthly air temperature of 18 °C (Table 3.2). Although air temperature can be as high as 33 °C on this site during the growing season, the temperature is a limiting factor for crop production during the fall and winter periods.

**Table 3.2** Total precipitation, monthly mean air temperature and record daily high temperature on the study site compared with 30-year average for the region, Carberry, Manitoba, Canada for the period 2011, 2013 and 2014 (Environment Canada 2014).

| | Total Precipitation | | | | Mean Temperature | | | | Record Daily High Temperature | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Month** | **2011 †** | **2013** | **2014** | **30 yr** | **2011** | **2013** | **2014** | **30 yr** | **2011** | **2013** | **2014** | **30 yr** |
| | ---------------------- (mm) -------------------- | | | | ------------------ (°C) ---------------------- | | | | ----------- (°C) -------------- | | | |
| January | M | 6.8 | 13.1 | 20.0 | -18.6 | -16.9 | -19.3 | -19.2 | 0.4 | 0.5 | 5.4 | 5.2 |
| February | M | 2.8 | 9.2 | 34.0 | -15.5 | -13.7 | -21.1 | -10.4 | 5.2 | 1.4 | -0.3 | 7.7 |
| March | M | 9.1 | 7.3 | 30.0 | -11.5 | -13.4 | -12.1 | -6.8 | 3.3 | 4.4 | 4.5 | 16.3 |
| April | 7.4 | 9.4 | 39.8 | 19.0 | 2.1 | -4.0 | -0.3 | 3.2 | 19.3 | 13.4 | 15.9 | 27.8 |
| May | 67.2 | 84.2 | 71.4 | 70.0 | 9.6 | 10.5 | 10.8 | 9.9 | 25.8 | 29.4 | 33.4 | 31 |
| June | 88.4 | 72.6 | 135.5 | 84.0 | 16.0 | 16.7 | 15.8 | 15 | 29.5 | 28.2 | 27.6 | 34.7 |
| July | 58.2 | 68.2 | 24.8 | 77.0 | 19.0 | 17.7 | 17.7 | 17.8 | 32.9 | 29.4 | 30.8 | 31.8 |
| August | 8.4 | 68.8 | 105.4 | 64.0 | 18.5 | 17.8 | 17.9 | 17.9 | 33.9 | 32.4 | 31.5 | 34 |
| September | 23.4 | 51.0 | 43.9 | 53.0 | 13.2 | 15.3 | 12.5 | 11.8 | 30.4 | 32.8 | 33.7 | 33.4 |
| October | 7.0 | 34.0 | 1.6 | 32.0 | 8.4 | 3.8 | 6.3 | 4.8 | 30.8 | 21.8 | 20.5 | 28.6 |
| November | 11.0 | 5.7 | 7.7 | 25.0 | -4.0 | -5.7 | -9.1 | -6.0 | 13.0 | 10.3 | 8.6 | 19.3 |
| December | 4.1 | 8.1 | 1.2 | 22.0 | -8.1 | -20.3 | -9.8 | -13.8 | 3.5 | 1.4 | 3.9 | 7.5 |
| **Total** | **275.1** | **420.7** | **460.9** | **530.0** | | | | | | | | |
| **Average** | | | | | **2.4** | **0.6** | **0.8** | **2.0** | | | | |
| **Max** | | | | | | | | | **33.9** | **32.8** | **33.7** | **34.7** |

† M indicate missing values from weathers station.

### 3.4.2 Nitrous Oxide Flux and Cumulative Emission

$N_2O$ emission varied daily and seasonally on the treatment across the 3 years. $N_2O$ fluxes peaked one to two weeks following manure or fertilizer application, which sometimes coincided with rainfall events (Figure 3.1). $N_2O$ fluxes were more pronounced in the first 3 weeks following N application, after which $N_2O$ fluxes diminished to a low level (below 5 g $N_2O$-N $ha^{-1}d^{-1}$) except for few spikes that occurred following heavy rainfalls.

When the daily $N_2O$ fluxes were aggregated to cumulative emission for an individual growing season, I observed that growing season cumulative $N_2O$ emission was significantly less on LPM compared to FER treatments ($p < 0.0001$) in two out of the three years presented. In both 2011 and 2014, the cumulative emissions from FER were 1.5 and 1.7-fold greater than those from LPM (Table 3.4), but in 2013, the cumulative $N_2O$ flux during the growing season on FER was not significantly different from LPM treatments. Cumulative growing season $N_2O$ flux was consistently low on the CON plots throughout the study period 0.18 – 0.19 kg N $ha^{-1}$.

**Table 3.3** Effect of nitrogen (N) source treatments and year on cumulative $N_2O$ emission, emission intensity and emission factors (EF).

| Year | Effect[a] | Cumulative Emission | Emission Intensity | EF_Total N | EF_Total_Available N |
|---|---|---|---|---|---|
| | **N_Source** | | | | |
| | CON | 0.19c | 0.14b | | |
| | FER | 1.21a | 1.15a | 1.09a | 1.09a |
| | LPM | 0.80b | 0.36b | 0.44b | 0.55b |
| | **Year** | | | | |
| | 2011 | 0.78a | 0.96a | 1.09a | 1.12a |
| | 2013 | 0.78a | 0.13b | 0.82ab | 0.85ab |
| | 2014 | 0.64a | 0.56a | 0.40b | 0.49b |

| Model Effect | | df | Pr > F | | df | Pr > F | |
|---|---|---|---|---|---|---|---|
| | N_treatment | 2 | <0.0001 | <0.0001 | 1 | 0.0002 | 0.0019 |
| | Year | 2 | 0.4968 | <0.001 | 2 | 0.0039 | 0.0106 |
| | Year X N_treatment | 4 | 0.0329 | 0.0036 | 2 | 0.0240 | 0.0148 |

**Note:** Least Square means with the same letter under N_Source or Year are not significantly different (Alpha=0.05).

[a]N_Source treatments, CON = unamended control, FER = Urea Fertilizer LPM =Liquid Pig Manure

**Table 3.4** Cumulative nitrous oxide flux, emission factors, emission intensity and grain yield from the control (CON), liquid pig manure (LPM) and urea fertilizer (FER) treatment plots during each growing season of the study. Soil nitrate and ammonium corresponds to average measurements from the treatments across each growing season.

| **Year (crop)** | **Treatment** | **Cumulative $N_2O$ †** (kg N ha$^{-1}$) | **Soil nitrate** mg N kg$^{-1}$ | **Soil ammonium** mg N kg$^{-1}$ | **Grain yield** (Mg ha$^{-1}$) | **Plant N Uptake** (kg N ha$^{-1}$) | **Emission intensity †** (kg $N_2O$-N Mg$^{-1}$ of yield) | **$N_2O$ emission factor Total N †** (% kg N kg$^{-1}$ N) | **$N_2O$ emission factor Total Available N †** (% kg N kg$^{-1}$ N) |
|---|---|---|---|---|---|---|---|---|---|
| **2011** | CON | 0.18*b* | 37.88*b* | 2.34*b* | 0.750*b* | 36*b* | 0.24*b* | | - |
| (Wheat) | FER | 1.54*a* | 52.91*a* | 7.96*a* | 0.801*a* | 52*ab* | 1.92*a* | 1.70*a* | 1.70*a* |
| | LPM | 0.62*b* | 37.93*b* | 2.39*b* | 0.881*a* | 56*a* | 0.70*b* | 0.48*b* | 0.55*b* |
| **2013** | CON | 0.19*b* | 11.37*c* | 0.76*b* | 3.130*b* | 75*b* | 0.06*b* | | - |
| (Barley) | FER | 1.00*a* | 52.39*a* | 2.56*a* | 5.909*a* | 209*a* | 0.18*a* | 0.45*a* | 0.45*a* |
| | LPM | 1.14*a* | 37.74*b* | 0.94*b* | 7.311*a* | 222*a* | 0.16*a* | 0.35*a* | 0.53*a* |
| **2014** | CON | 0.19*c* | 12.29*b* | 1.18*b* | 1.33*b* | 65*a* | 0.11*b* | | - |
| (Wheat) | FER | 1.09*a* | 26.10*a* | 4.32*a* | 2.43*a* | 90*a* | 1.34*a* | 1.13*a* | 1.13*a* |
| | LPM | 0.64*b* | 24.69*a* | 1.23*b* | 2.927*a* | 112*a* | 0.22*b* | 0.50*b* | 0.57*b* |

† LS-means with the same letter within a column for a given year are not significantly different (Tukey-Kramer groupings, alpha=0.05).

### 3.4.3 Grain Yield, Nutrient Uptake, Emission Factor, Emission Intensity and Soil N

Grain yield was generally low on the study site with lowest yield recorded in 2011 for wheat (<1 Mg $ha^{-1}$) which was far lower than the provincial average for the same year (2.3 Mg $ha^{-1}$). But 2014 wheat yield was not as low as 2011 (Table 3.4). Year 2013 was a bounty harvest with barley yield ranging from 3 to 7 Mg $ha^{-1}$ (Table 3.4). The yield from the N treated plots (LPM and FER) were significantly greater than the unamended control plot (CON). In all the three years, crop yield and nitrogen uptake were marginally greater on the LPM treatments than the FER by values ranging from 5 to 20 %, although not significantly different (Table 3.4).

Available nitrogen was high in the soil following the application of FER and LPM, particularly within the first two weeks. The growing season average soil N data ($NO_3^-$-N and $NH_4^+$-N) is presented in Table 3.4. Soil nitrate was higher on FER plots than LPM plots in 2011 and 2013 but not in 2014 (Table 3.4). Generally, soil nitrate was low on the treated plots in 2014 than in 2013. Soil $NH_4^+$-N was high the first few days after N application, but this did not persist for long in soil. On the other hand, a large amount of soil $NO_3^-$-N was measure in soil for a long period, more than a month following N application (Figure 3.1). In all the three years, soil $NH_4^+$-N was consistently greater on FER than LPM treatments (Table 3.4).

Nitrous oxide emission factor and emission intensity were significantly lower on the LPM plots than FER plots (Table 3.3). There was a significant interaction between year and treatment applied (Table 3.3). The emission factors calculated based on total N and total available N applied in 2011 from FER were three times greater than that of LPM (Table 3.4). While in 2013, the emission factor from FER was not significantly different from that of LPM. Also, in 2014, the emission factor from FER was more than two times greater than that of LPM. The emission intensity followed a similar trend as the emission factor (Table 3.4), with FER having a higher emission intensity compared to LPM across all the years. In 2011 for every 1000 kg of wheat grain produced, only 0.7 kg of $N_2O$-N was lost from LPM, in contrast to about 2 kg of $N_2O$-N lost from FER the same year. Similarly, in 2014, for every 1000 kg of wheat produced, 0.2 kg of applied N was lost as $N_2O$ on LPM in comparison to 1.3 kg of applied N lost on FER as $N_2O$.

**Table 3.5** Pearson's correlation showing the relationship between soil temperature, soil moisture, soil nitrate-nitrogen and natural log-transformed $N_2O$ flux.

| | ln ($N_2O$ flux) | | |
|---|---|---|---|
| **Treatment** | **Soil temperature** | **Soil moisture** | **Soil nitrate-nitrogen** |
| CON | -0.03ns | 0.37*** | 0.13** |
| FER | 0.34*** | 0.35*** | 0.34*** |
| LPM | 0.33*** | 0.40*** | 0.33*** |

Note: *** indicates significance at 1%, ** indicates significance at 5%, ns indicates not significant. Treatments are Liquid Pig Manure (LPM), Urea fertilizer (FER) and Un-amended control (CON).

**Table 3.6** Regression model evaluating the effect of soil nitrogen, soil temperature and soil moisture on $N_2O$ flux.

| **Treatment** | **Regression model** | $R^2$ | **RMSE** (kg N $ha^{-1}$ $d^{-1}$) | **Dependent mean** | **P** |
|---|---|---|---|---|---|
| CON | Log $N_2O$ = -1.8 + 0.005 N + 0.003 T + 0.114 W | 0.15 | 1.48 | -0.10 | <0.0001 |
| FER | Log $N_2O$ = -5.0 + 0.010 N + 0.152 T + 0.177 W | 0.39 | 1.54 | 1.39 | <0.0001 |
| LPM | Log $N_2O$ = -4.7 + 0.009 N + 0.136 T + 0.177 W | 0.38 | 1.50 | 1.14 | <0.0001 |

Note: N is soil nitrate-nitrogen (mg N $kg^{-1}$), T is soil temperature (°C), W is soil gravimetric soil moisture content (%). Treatments are Liquid Pig Manure (LPM), Urea fertilizer (FER) and Un-amended control (CON).

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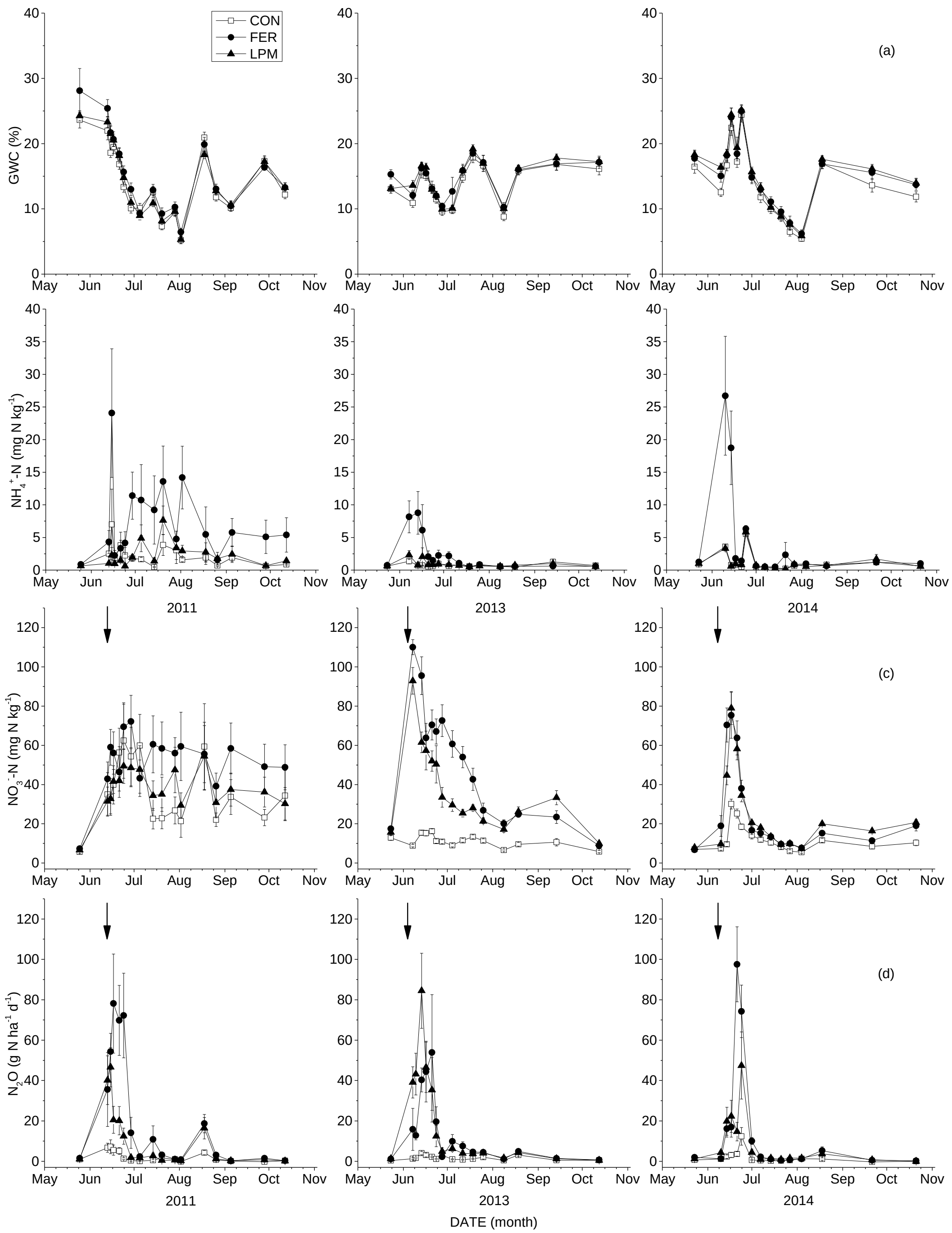


**Figure 3.1** Gravimetric soil moisture (0-10 cm soil depth) (a), soil ammonium (b), soil nitrate (c), and nitrous oxide flux (d) from liquid pig manure (LPM), urea fertilizer (FER) and control (CON) treatments. Values are means (n = 12) ± SE. An arrow indicate the day of N application on 26th June 2011, 17th June 2013, and 11th June 2014.

## 3.5 Discussion

### 3.5.1 Crop Yield and Nitrogen Uptake

Crop yield and crop N uptake were marginally higher on LPM compared to FER treatments although not significantly different. This might be because, as opposed to urea, manure contains other essential plant nutrient than N that contributed to promote the crop growth and nutrient uptake (Karimi and Akinremi 2018; Nikièma et al. 2013). This difference might come from the fact that N input could have been higher in the manure than the urea plots. Note that LPM was applied based on available N content (Table 3.1). The yield responds to N source type suggest that liquid manure had a marginal crop yield and N uptake advantage over urea fertilizer. One may attribute this to the fact that LPM contains other plant essential nutrient compared to urea which only has N. The yield response also affected the $N_2O$ emission intensity on the study site.

The yield response observed in all treatments receiving N, either in the form of manure or urea in all years strongly suggests that soil moisture was limiting on the loamy sand soil. Crop yield was low in 2011 compared to 2013 and 2014. Although there was low yield in the entire province in 2011 (Yield Manitoba, 2012), the average wheat yield on the study site, 0.8 Mg ha$^{-1}$ was far below the provincial average yield of 2.3 Mg ha$^{-1}$. The low yield in 2011 was ascribed to low precipitation on the study site that year. Due to the sandy nature of the soil, moisture and nutrient are easily lost to leaching (Karimi and Akinremi 2018). The low crop yield in 2011 affected the emission intensity as higher emission intensity were observed in 2011 compared to other years most especial year 2014 which also had wheat crop. In all three years of the study, the un-amended plots had significantly lower crop yield than the amended ones. The results clearly indicate that the crops responded positively to N addition, but the magnitude of the yield response was not influenced by the N amendment type (Table 3.4).

### 3.5.2 Nitrous Oxide Emission, Emission Factor, and Emission Intensity

As expected, the results clearly indicate that N fertilization had an impact on both the daily and cumulative $N_2O$ fluxes. The daily fluxes were low in all treatments prior to N fertilization, but sharply increased on both the FER and LPM plots relative to control (Figure 3.1). The increase reached a pick after a few days/ weeks, then quickly decreased to the CON after a while, and remained low for the rest of the growing seasons, with the exception of a moderate spike that occurred in late August/ early September of 2011. The spikes that occurred following treatment application was also accompanied by elevated soil available N level. Manure and urea were applied the same day when the plots were plowed to kill weed and seed the crop. The few days following N application and seeding, vegetation occupancy on the plots was certainly low, and soil N availability must have exceeded the ability of the little crop to take it up, at least during this period. Previous studies have shown that $N_2O$ emissions from soil occur when N availability in soil exceed crop demand most especially when N source is recently added (Signor et al. 2013). But as the crop gets well established over the course of the growing season, N uptake by the crop increases, thus reducing N loss through emissions. The small spike that occurred late in the growing season, particularly in 2011, coincided with a spike in soil moisture level from certainly a rainfall event, this indication that N availability is not the single factor required to stimulate $N_2O$ flux.

The daily and cumulative $N_2O$ fluxes not only increased following N addition in soil, but also N fertilizer source had a significant impact on these fluxes. Some daily and annul growing season cumulative $N_2O$ fluxes were higher in the FER treatment relative to the LPM treatment (Figure 3.1 Table 3.4). Also, the overall growing season cumulative emission showed that cumulative $N_2O$ fluxes were significantly lower on LPM compared to FER treatments (Table 3.3). We know that $N_2O$ emissions is significantly driven by N availability in soil. It is possible that N volatilization from LPM must have exceeded 25% of applied manure N, thus leaving less available N in the LPM soil that can be subjected to $N_2O$ emissions (Lasisi et al. 2020; Lasisi et al. 2019; Rochette et al. 2008). The lower soil available level and $N_2O$ flux from the LPM plots relative to the FER plots provide strong evidence of this.

The source of N regarding LPM vs. FER affected $N_2O$ flux in this study. Fluxes were significantly less on LPM than FER. There was a significant year by treatment interaction. As seen in Table 3.4 annual cumulative growing season emission was significantly low on LPM that FER except in 2013. This exception may be attributed to environmental factor and or the amount of manure applied that year. Application rate of LPM varied annually due to difference in the dry matter content and N content in the manure. This varying N rate eventually affected $N_2O$ flux from the treatments. Cumulative growing season $N_2O$ Fluxes were on LPM both low in 2011 and 2014 when applied N was low in 2013 when applied LPM was high, about three times greater than those applied in 2011 and 2014 (Table 3.1 and Table 3.4). The pattern of $N_2O$ flux from treatments in the current study is comparable with those in previous studies (Asgedom et al. 2014; Nikièma et al. 2016). In a study carried out on clay soil in southern Manitoba, Asgedom et al. (2014) reported lower cumulative nitrous oxide flux from solid dairy manure compared to urea fertilizer, which they attributed to lower nitrogen release from manure relative to the fertilizer. Similarly, Chantigny et al. (2010) reported that more than 6% of the applied N from mineral fertilizer was lost as $N_2O$ compared to 3-5% from liquid pig manure when applied to clay soil. On the contrary, Petersen (1999) reported higher $N_2O$ flux from untreated LPM in comparison with FER.

Nitrous oxide emission factor and emission intensity were significantly lower on LPM compared to FER. For instance, in 2011, only 0.5% of applied N was lost as $N_2O$ on LPM compared to 2% from FER in the same year. Similarly, in 2014, only 0.5% of applied N was lost as $N_2O$ from LPM, compared to 1.1% of applied N from FER in the same year. These emission factors are similar to those reported by (Adelekun et al., 2019; Lazcano et al., 2016) which ranged between 0.5 and 2.0% of the applied N. The difference in emission factor between LPM and FER in the present study may also be attributed partly to applied N in manure and ammonia volatilization. As observed in the current study, the $N_2O$ emission factor varies from year to year based on the amount of N applied, N source and environmental conditions Lesschen et al. (2011).

The carbon content in the manure might have contributed to the increase of the $N_2O$ flux on LPM compared to FER in 2013, especially considering the relatively high solid content of the manure (Table 3.1). Soluble carbon serves as a substrate for microbial communities that favours the nitrification and denitrification process. Velthof et al. (2003) reported that easily mineralizable carbon was one of the major factors that affected $N_2O$ emission from LPM compared to FER in their study. In the current study, LPM treatments have been receiving a continuous annual application of manure since 2009. Each year, I assumed that only 25% of the organic N is mineralizable. If I take into cognisant the C content in the remaining 75% portion, this may likely result in a significant build-up of organic carbon which in essence may affect $N_2O$ emission from the LPM which was magnified in 2013 due to additional N content (Edmeades, 2003; Lazcano et al., 2016).

Environmental factor has a major influence on cumulative $N_2O$ emission, emission factor and emission intensity on the study site. Apart from applied manure composition, the main the main distinguishing factor from one year to another is the environmental condition. Year 2013 was a wet year as compared to 2011 (Table 3.2) with annual precipitation of 420 mm as compared with 225 respectively. As a result, the favourable moisture in soil coupled with high N content applied that year did not yield lower $N_2O$ flux on LPM compared FER as seen in other years. Although, year 2014 was also wet, the amount of N applied that year was not high enough as to have caused high $N_2O$ flux. Smith and Owens (2010) pointed out that $N_2O$ flux were greater from manure treatment during wet period. It can thus be inferred that the main factors that contribute to N2O flux are the environmental conditions and applied N content in soil.

### 3.5.3 Effect of Soil Temperature, Soil Moisture and Available Nitrogen on $N_2O$ Emission from LPM and FER

The correlation analysis (Table 3.5) showed that soil moisture and soil nitrate-nitrogen were strongly and positively correlated with $N_2O$ flux from LPM and FER. The regression analysis (Table 3.6) equally revealed that up to 39% of the variations in $N_2O$ fluxes from LPM and FER could be explained by variations in soil temperature, soil moisture and soil nitrate. This agrees with the report of Lazcano et al. (2016), who also observed that about 39% of the variability in $N_2O$ flux was explained by variations in soil temperature, soil moisture content and soil available nitrogen on agricultural soil fertilized with liquid manure and inorganic fertilizer. However, for CON plots, $N_2O$ flux was only significantly correlated with $NO_3$-N at 5% significance level and the Pearson's correlation of 15% was smaller than those treatments with N applications (Table 3.4). This is an indication that the application of N greatly influenced $N_2O$ emissions from this study.

Soil moisture and soil nitrogen content were two important factors that affected nitrous oxide emission from soil following application of N when the temperature was not limiting. The year 2011 was warm with a relatively high $N_2O$ flux compared to 2014. The year 2011 was also dry compared to 2014 in terms of total precipitation; this led to a 3-fold reduction in wheat yield compared to 2014. This dryness in 2011 did not decrease $N_2O$ emission but increased the emission intensity due to poor yield on the site. One may attribute the high flux in 2011 to the wet soil when manure and fertilizer were applied as a result of the antecedent effect of the wet year 2010. In June, when soil moisture was high, resulting from frequent and high rainfall events (Figure 3.1), $N_2O$ fluxes were high and coincided with the time of N application. Between July and August 2011, soil moisture content declined, and this resulted in negligible $N_2O$ flux at this period. Soil moisture affects nitrification and denitrification processes in soil and $N_2O$ flux from it. Soil moisture also plays an important role in regulating soil oxygen level, which in turn affects the use of nitrate as an alternate electron acceptor. At the end of August, episodic rainfall events also increased $N_2O$ flux, although not as high as shortly after N treatment application in June.

Nitrogen input and availability are highly linked to $N_2O$ flux on agricultural soils. When available N input in the soil is in excess of plant demand, $N_2O$ flux tends to increase (Jarecki et al. 2008). In the current study, high $NO_3^-$-N and $NH_4^+$-N from FER in 2011 and 2014 led to increased $N_2O$ flux compared to LPM (Figure 3.1 and Table 3.4), because the N was transformed in soil before crops could take it up. Hydrolysis of urea leads to the production of high $NH_4^+$-N in the soil, thus providing the necessary substrate for nitrification and the release of $N_2O$ through the nitrification process. The rate of release of $NH_4^-$-N, and subsequently nitrate, from FER, differs from LPM. Up to 80% of the total nitrogen in the LPM is in $NH_4^-$-N form, but this is not instantly made available in soil for plant use as some are immobilized by microorganism while the rest is in an organic form that is gradually released for crop uptake. Ige et al. (2015) reported a higher amount of inorganic N mineralization from FER compared to LPM. They attributed the difference to immobilization of N. The $NH_4^+$-N from applied LPM and hydrolysis of urea is soon transformed to nitrate, which serves as a substrate for the denitrification process, in the presence of favourable soil moisture and other environmental conditions.

## 3.6 Conclusion

This study was conducted to compare $N_2O$ flux from LPM and FER applied to annual crops on a sandy loam soil. I reported that $N_2O$ flux from LPM was significantly less than that from FER. There was a significant year by treatment interaction which indicated that apart from applied N content which varied from year to year based on manure composition, environmental factor such as precipitation was also major factor that affected flux of $N_2O$ from the study site. Crop yield and N uptake were marginally higher on LPM treatment compared to FER, although not significantly different. In all the three years, emission factor from LPM (~0.5%) was lower than that of FER (ranged between 1.1 and 1.7%). The results clearly suggest a $N_2O$ emission reduction benefit and a marginal crop yield advantage of LPM over FER. Soil nitrate N, soil temperature and soil moisture content explained up to 40 % of variations of $N_2O$ fluxes in this study, as evidenced in the regression analysis results. More so, these factors were positively and strongly correlated with $N_2O$ emissions and thus considered principal factors that influenced $N_2O$ emission in this study asides applied N.

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# 4. SOIL MOISTURE AND NITROUS OXIDE FLUXES FROM PERENNIAL FORAGE GRASSES AND ANNUAL CROPS RECEIVING MANURE - A MODELLING APPROACH USING DNDC


## 4.1 Abstract

Well-validated process-based models are an indispensable tool for estimating greenhouse gas fluxes from agricultural soils. They can be used to assess crop and nutrient management efficiencies, which are important for mitigating $N_2O$ emission. The objective of this study was to evaluate the DeNitrification-DeComposition model (DNDC v.Can) in simulating $N_2O$ fluxes and moisture contents from soils amended with liquid (LPM) or solid (SPM) pig manures and cropped to perennial forage (FPP) and annual (ANN) crops. A sensitivity analysis of the model was also carried out. The result from the sensitivity analysis showed that soil moisture output from the model was more sensitive to field capacity with a relative sensitivity index (RSI) of 1.73, while the model was insensitive to hydraulic conductivity (RSI = 0.04). Nitrous oxide output was moderately sensitive to soil organic carbon content with RSI of 1.0. Average daily soil moisture content expressed as water-filled pore space estimated using the DNDC v.Can compared moderately well with field observed values on ANN plots than FPP plots (RMSE < 0.1 % WFPS, NRMSE < 27%, NSE > 0.5 and ME < 0.04 % WFPS). However, the model limit water flow to field capacity through the cascade approach thus rendering the hydraulic conductivity function useless in the model. Modelled daily $N_2O$ flux had a better fit with field observed $N_2O$ flux on ANN plots (RMSE < 0.014 kg N $ha^{-1}$, NRMSE < 30% and ME < 0.005 kg N $ha^{-1}$) than on the FPP plots. I observed that crop management affected soil moisture, which in turn affected the $N_2O$ flux. Despite the wide use of the wide use of the DNDC model, some area of the model still need work

such as the FPP. A review of the water flow subroutine in the DNDC is recommended to eliminate the use cascade approach in limiting water flow and let water retention and hydraulic conductivity function deter flow of water; this should result in a better environmental quantification of management practices that affect $N_2O$ fluxes.

## 4.2 Introduction

Understanding the process of greenhouse gas production is a key to control its emission in our environment. Computer model simulations that accurately estimate the flux of greenhouse gases (GHG) shows the extent of our understanding of its emission processes. Nitrous oxide ($N_2O$) is a powerful GHG, capable of depleting the ozone layer (IPCC 2014). There is an increasing trend in the anthropogenic emission of $N_2O$ recently. According to IPCC (2014a), global $N_2O$ concentration in the atmosphere was around 320 ppb in 2014 and is increases at an annual rate of 0.73 ppb. The flux of these gases is affected by farm management practices on agricultural soils.

The choice of source of nitrogen; liquid pig manure (LPM) vs. solid pig manure (SPM) or crop management; perennial forage grasses vs. annual crops may influence the soil physico-chemical properties and moisture-holding capacity of a soil which in turn affects the flux of $N_2O$ gas (Adesanya et al. 2016; Nikiema et al. 2016). Liquid pig manure contains high water content, sometimes up to 99 percent. It is obtained from washed off feces, urine and other wastes in pig barns and are sometimes stored in lagoons. It also has high ammonium content. On the other hand, solid pig manure is obtained from a dung pile containing a mixture of straw beddings, feces, urine, and other animal wastes. Compared to LPM, SPM has lower water content, an average of 75 % and has a higher carbon to nitrogen (C:N) ratio. Land application of manure is considered a safe way to dispose of the waste from these animals. However, when these manures are applied at rates that supply more nutrients than the plant demand, nutrients in manure can be lost in the form of leaching (Singh et al. 2019), runoff (Jokela et al. 2016) or gaseous emissions (Adelekun et al. 2019). Thus, the need to manage the form and source of nutrient application.

Perennial forage grasses offer a better way to manage GHG fluxes on agricultural land compared to annual crops. According to Maas et al. (2013), the inclusion of perennial forage grasses in crop rotation may help conserve soil organic matter while minimizing nitrous oxide fluxes to the environment. Timothy and Orchard grasses are commonly grown forage grasses or non-leguminous hay on the Canadian prairie for feeding livestock. These grasses are perennial in nature; they have fibrous roots which contains high carbon content. They tend to improve soil structure and organic matter content compared to regular annual crops (Adesanya 2015). Drewer et al. (2012) observed less GHG fluxes from perennial forage grasses compared to annual crops. Mielenz et al. (2017) modelled conversion of pasture to annual crops; they observed that $N_2O$ flux was high on the wheat plots in the first year after the conversion. On the other hand, Senapati et al. (2016) used the Daycent model to estimate $N_2O$ flux from fertilized forage grass and annual crop; they observed a 59% increase in $N_2O$ emission from the fertilized forage grass compared to annual crop that was also fertilized. Properly calibrated and validated models are useful tools because they can be used to run simulation scenarios (Smith et al. 2020).

DNDC is a widely adopted model that is actively being developed. There are several members of the DNDC extended family; these include UK-DNDC (Brown et al. 2002); NZ-DNDC (Saggar et al. 2004); LANDSCAPE-DNDC (Haas et al. 2012); DNDC-EUROPE (Britz et al. 2004); FOREST-DNDC-TROPICA (Kiese et al. 2005); DNDC-RICE (Li et al. 2004); BE-DNDC (Beheydt et al. 2007); DNDC-CAN (Kröbel et al. 2011); NEST-DNDC (Zhang et al. 2012); Manure DNDC (Li et al. 2012). Most of these are regionalised for optimal performance in different climates while others are optimised for different crop and nutrient management. The DNDC-CAN is a regionalised version of the DNDC model specifically optimized for crop and nutrient management practices of Canadian cool and temperate climates (Kröbel et al. 2011).

Kröbel et al. (2011) developed the crop growth module of the DNDC model using Canadian spring wheat and reported that the model performed well in simulating plant biomass, nitrogen and carbon in the soil but suggested the need for model improvement to capture soil layer parameters. Smith et al. (2013) assessed the effect of climate change on crop production and GHG emission in Canada using the DNDC model. In a study carried out at TGAS MAN which is in Manitoba, Uzoma et al. (2015) used the DNDC model to assess the effect of agricultural management practices on $N_2O$ flux. They observed that the model overestimated $N_2O$ flux from alfalfa production. They equally observed that DNDC simulated soil moisture content better in wet years than in dry years and that the model tended to underestimate nitrous oxide during long period of episodic rainfall. They attributed this to the inability of the model to consider water flowing through clay cracks and the cascade approach to water flow employed by the model. Therefore, they suggested an improvement to the hydraulic routine of the model. He et al. (2016) also used the DNDC model to estimate the impact of climate change on crop yield and $N_2O$ emission in Southern Ontario. They observed that the model overestimated $N_2O$ flux from no-till systems compared to conventional tillage, which they attributed to the overestimation of soil available nitrogen and underestimation of soil moisture during the dry year. Congreves et al. (2016) and Dutta et al. (2016a) worked to improve ammonia volatilization from inorganic fertilizer and manure, respectively, in the model. Dutta et al. (2016b) incorporated the FAO Penman-Monteith equation in the DNDC model to improve evapotranspiration in the model. Soil temperature and thermal conductivity of the model was improved by Dutta et al. (2018), and they also incorporated the effect of crop canopy and residue cover on the soil in the model. More recently, Smith et al. (2020) extended the soil profile depth to 2 m and added capability of including heterogeneous soil layers.

Steps have been taken over the years to improve various aspects of the model from evapotranspiration to soil temperature (Congreves et al. 2016; Dutta et al. 2016a; Dutta et al. 2016b;

Dutta et al. 2018; Kröbel et al. 2011; Smith et al. 2013) but little effort has been made to validate this model on managed manured grasslands in the Prairie region of Canada. The objectives of this study were to (i) evaluate the performance of the DNDC v.Can model in simulating soil moisture and nitrous oxide emissions from perennial forage grasses and annual crops that were amended with solid and liquid pig manure. (ii) Carryout out a sensitivity analysis of the model with respect to soil moisture and $N_2O$ flux.

## 4.3 Materials and Methods

### 4.3.1 Site Description

The data used in this modelling study was derived from a field experiment conducted by Adelekun et al. (2019) located at the University of Manitoba Ian N. Morrison Research Farm, Carman, Manitoba, Canada (49° 29.619'N, 98° 2.204'W, 266.1 m asl). In Manitoba, air temperature ranges from a low of -35°C in the winter period to a high of 36°C in the summer period, with July being the warmest period of the year. The average annual precipitation is about 545 mm over a 30-year period (1981-2010), the majority of which falls as rainfall from May to October. The soil type on the study site is sandy loam, Hibsin soil series, Orthic Black Chernozem according to the Canadian system of soil classification, this can be mapped as Mollisol according to the USDA system of soil classification (Agriculture and Agri-Food Canada 1998; Mills and Haluschak 1993). The soil's pH ranged from 6.2 – 6.8, while the soil bulk density is about 1.2 $Mg/m^{-3}$ at 0 to 15 cm soil depth (Mills and Haluschak 1993; Adesanya 2015; Adesanya et al. 2016). It is a well-drained soil with a very gentle slope of fewer than five degrees.

### 4.3.2 Data Used in Model Calibration and Validation

A detailed procedure of data collection and measurements of data used in calibration and validation of the model in this study has been described in chapter 2 of this dissertation. Further references are also available in reports of Adelekun et al. (2019), Nikièma et al. (2016) and Karimi et al. (2017). The experimental design was a split-plot design with two cropping systems as the main plot; regular annual crops (ANN) and perennial forage grasses (FPP), while the subplots comprise of three manure treatments; solid pig manure (SPM), liquid pig manure (LPM), and un-amended control (CON) plots. The annual plot was a rotation of barley (*Hordeum vulgare* variety Tradition) and canola (*Brassica napus* L.), while the FPP was a combination of timothy (*Phleum pratense* L. variety Promesse) and orchard forage grasses (*Dactylis glomerata* L. variety AC Nordic) in ratio 68% to 32% respectively except in 2013 when the FPP was seeded to canola. Each treatment was replicated four times. Each plot measured 10 m by 10 m (100 $m^2$). Liquid pig manure or solid pig manure were applied each year to all the plots except the control plots (Table 4.1). The manure composition and quantity were applied to each treatment plot as shown in Table 4.1. The ANN was tilled annually using tandem disc plow up to a depth of 10 cm to incorporate the manure applied, while the FPP was not tilled except in the fall of 2012 when the forage grasses were plowed down (Table 4.3).

$N_2O$ flux samples were collected using the static vented chamber technique. Each gas chamber measures 20.3 cm in diameter with a height of 10 cm. Before the first sampling, gas chambers were deployed at least a day before measurement, after which chambers were left on the field throughout the sampling period, except when there was a major mechanical operation on the field that required the chambers to be moved e.g., harvesting and herbicide application. Gas samples were collected from May to October each year from 2011 to 2014. Gas samples were collected on 15 sampling dates each year. Each year, before manure treatment application, one sample was collected as basal measurement. Immediately after the manure treatment application, samples were collected at the rate of three samples per week for the first three weeks, after which sampling frequency reduced to one sampling per week for the next month. The samples were taken fortnightly for the next month, and finally, sampling was reduced to once per month. On each sampling occasion, soil samples were collected around each chamber to a depth of 10 cm for soil moisture. Also, on each sampling occasion, soil temperature was taken around each chamber to a depth of 2.5 cm.

**Table 4.1** Manure content and application rates on the study site at Carman.

| Year | Sys | Manure treatment | Manure Parameters | | | | | Application Rates | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Moisture content | % Total N in manure (Wet) | $NH_4^+$ and $NO_3^-$ in manure | Organic N in manure | Manure C:N ratio | ^x^Applied manure | Applied organic C | *Applied $NH_4^+$ and $NO_3^-$ | Applied organic N | Applied total N |
| | | | | (%) | (ppm) | % | | L ha$^{-1}$ or kg ha$^{-1}$ | kg C ha$^{-1}$ | kg N ha$^{-1}$ | kg N ha$^{-1}$ | kg N ha$^{-1}$ |
| 2011 | ANN | CON | | | | | | | | 0 | 0 | 0 |
| | ANN | LPM | 0.97 | 0.32 | 2657 | 0.054 | 4 | 31488 | 419 | 84 | 17 | 101 |
| | ANN | SPM | 0.78 | 0.66 | 2077 | 0.452 | 14 | 61000 | 5827 | 127 | 276 | 403 |
| | FPP | CON | | | | | | | | 0 | 0 | 0 |
| | FPP | LPM | 0.97 | 0.32 | 2657 | 0.054 | 4 | 62998 | 837 | 167 | 34 | 202 |
| | FPP | SPM | 0.78 | 0.66 | 2077 | 0.452 | 14 | 74000 | 7069 | 154 | 335 | 488 |
| 2012 | ANN | CON | | | | | | | | 0 | 0 | 0 |
| | ANN | LPM | 0.90 | 0.55 | 3658 | 0.184 | 8 | 36400 | 1613 | 133 | 67 | 200 |
| | ANN | SPM | 0.66 | 0.75 | 1553 | 0.595 | 20 | 43000 | 6348 | 67 | 256 | 323 |
| | FPP | CON | | | | | | | | 0 | 0 | 0 |
| | FPP | LPM | 0.90 | 0.55 | 3658 | 0.184 | 8 | 54410 | 2411 | 199 | 100 | 299 |
| | FPP | SPM | 0.66 | 0.75 | 1553 | 0.595 | 20 | 53000 | 7824 | 82 | 315 | 398 |
| 2013 | ANN | CON | | | | | | | | 0 | 0 | 0 |
| | ANN | LPM | 0.93 | 0.58 | 3509 | 0.232 | 5 | 19720 | 618 | 69 | 46 | 115 |
| | ANN | SPM | 0.75 | 0.73 | 273 | 0.701 | 15 | 21000 | 2280 | 6 | 147 | 153 |
| | FPP | CON | | | | | | | | 0 | 0 | 0 |
| | FPP | LPM | 0.93 | 0.58 | 3509 | 0.232 | 5 | 52460 | 1643 | 184 | 122 | 306 |
| | FPP | SPM | 0.75 | 0.73 | 273 | 0.701 | 15 | 73000 | 7927 | 20 | 511 | 531 |
| 2014 | ANN | CON | | | | | | | | 0 | 0 | 0 |
| | ANN | LPM | 0.99 | 0.16 | 1351 | 0.029 | 4 | 46470 | 288 | 63 | 13 | 76 |
| | ANN | SPM | 0.77 | 0.71 | 1350 | 0.571 | 14 | 20250 | 2057 | 27 | 116 | 143 |
| | FPP | CON | | | | | | | | 0 | 0 | 0 |
| | FPP | LPM | 0.99 | 0.16 | 1351 | 0.029 | 4 | 48260 | 299 | 65 | 14 | 79 |
| | FPP | SPM | 0.77 | 0.71 | 1350 | 0.571 | 14 | 16000 | 1626 | 22 | 91 | 113 |

### 4.3.4 Model Description and Package

The DeNitrification DeComposition (DNDC) model was first described by Li et al. (1992). It is a biogeochemical model for simulating nitrogen and carbon dynamics in the soil. The model uses ecological drivers such as climate, soil, vegetation, and farm management-practices to estimate soil climate, crop growth, and rate of decomposition, which are, in turn, used for estimating nitrification, denitrification and fermentation processes in soil. The current version of the DNDC is the DNDC 9.5. In this study, the soil environmental variables from the model include soil temperature, soil moisture, soil nitrate, and soil ammonium, while the trace gas estimated is $N_2O$. The version of DNDC used is the DNDC v.Can, which has been developed to handle biogeochemical processes in cool and temperate climates as Canada as affected by crop and nutrient managements. An overview of changes of DNDC v.Can to the original DNDC (Li et al., 1992) is given in Table 4.2. All updates on the model are published on the public web at the GitHub, https://github.com/BrianBGrant/DNDCv.CAN (Smith et al. 2013).

The water flow in the DNDC model was described by Li et al. (1992) as a one dimensional flow structure in which water retention and hydraulic conductivity is controlled by that of Clapp and Hornberger (1978) and Campbell (1974), respectively using a tipping bucket approach. In recent development, Smith et al. (2020) have introduced a new water retention curve and hydraulic conductivity into the DNDC v.Can which is that of Averjanov (1950) and Irmay (1954) in order to improve the water flow in the model, although this still use the tipping bucket approach. These 2 approaches of estimating water retention curve, Clapp and Hornberger, and Averjanov and Irmay were compared using optimised soil parameters in this study (Table 4.4).

Soil Moisture Flow: $Q = -K\frac{\partial h}{\partial z} \cong -K_{i,\,i+1} \times \frac{h_i - h_{i+1}}{z_i - z_{i+1}}$ [5]

Where $Q$= water flow rate (L $T^{-1}$); $K$ = hydraulic conductivity (L $T^{-1}$); $h$ = Matric head (L); $z$ = soil depth (L); $\theta$ = soil water content (L).

***Clapp and Hornberger***

$\psi = \psi_s W^{-b}$ [6]

$\psi = -m(W - n)(W - 1)$ [7]

$\theta_h = \frac{\theta_s}{\sqrt[b]{\frac{\psi}{\psi_s}}}$ [8]

If W< $W_i$ $\theta < W_i\,\theta_s$ [9]

$k = W^{2b+3}$ [10]

*Where* $\psi$= matric suction; b= empirical soil parameter (4 to 11.4); W = Volumetric water content or soil wetness $= \frac{\theta}{\theta_s}$; $K_h =$ unsaturated hydraulic conductivity; $K_s$ = saturated hydraulic conductivity; k = relative conductivity $= \frac{K_h}{K_s}$; $\theta$ = volumetric water content; $\theta_s$ = saturated volumetric water content = total porosity; $\psi_i$ = matric suction at inflection point; $\psi_s$ = water tension parameter (saturation suction); $W_i$ = Water content where retention curve has inflection (0.92); m = m1 = empirical soil parameter = $\frac{\psi_i}{(1-W_i)^2} - \frac{\psi_i b}{W_i(1-W_i)}$; n = m2 = empirical soil parameter = $2W_i - \left(\frac{\psi_i b}{mW_i}\right) - 1$, (Clapp and Hornberger 1978)

***Averjanov and Irmay***

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} \quad [11]$$

$$K_h = K_s S_e^n \quad [12]$$

$$K_h = K_s \left(\frac{\theta - \theta_r}{\theta_s - \theta_r}\right)^n \quad [13]$$

Where $K_h$ = unsaturated hydraulic conductivity (L $T^{-1}$); $K_s$ = saturated hydraulic conductivity (L $T^{-1}$); $\theta_r$ = residual water content ($L^3$ $L^{-3}$); $\theta_s$ = water content at saturation ($L^3$ $L^{-3}$); $\theta$ = volumetric water content ($L^3$ $L^{-3}$); $n$ = an empirical factor which is equal to 3.5.

**Table 4.2** Developmental changes in DNDC v.Can.

| Description of model development | Reference |
| --- | --- |
| Spring wheat sub-model for DNDC in Canada (Crop growth, N uptake, root growth, biomass partitioning, C:N ratio of biomass fraction) | Kröbel et al. (2011) |
| Ammonia volatilization from pig manure | Congreves et al. (2016) |
| Ammonia volatilization from inorganic fertilizers, urea hydrolysis | Dutta et al. (2016a) |
| Evapotranspiration, crop coefficient water extraction time, water use efficiency | Dutta et al. (2016b) |
| Soil temperature, thermal properties of soil, frozen conditions in soils, effect of canopy and residue cover on crop. | Dutta et al. (2018) |
| Tile drainage, soil nitrogen movement with runoffs, heterogenous soil layer, extending profile depth up to 2 m. | Smith et al. (2020) |

### 4.3.5 Model build up, boundary and initial conditions

The site scale in the DNDC model is a one-dimensional model that estimates soil thermal-hydraulic and nitrogen dynamics from a single point. The DNDC 9.5 has a maximum profile depth of 0.5 m with a spatial resolution of 0.05 m, in which moisture and temperature is assumed to be the same in the profile. soil moisture beyond the 0.5 m depth drains into the groundwater. The DNDC model employs a finite difference method to model moisture and temperature flow based on gradients of matric head and temperature, respectively. The recent development in the DNDC v.Can extended the profile depth to 2 m. This extension will allow plant with tap roots and high root density to extract moisture beyond the original 50 cm. The DNDC V.Can also allows for heterogenous properties of soil layers to be specified. The soil and crop parameters used in calibrating the model in this study was described in Table 4.4 *Optimized soil parameters used in plotting retention curve and hydraulic conductivity function for soil depth 0 - 10 cm.*

| **Description** | **Soil Parameters** | **Clapp and Hornberger** | **Averjanov and Irmay** |
|---|---|---:|---:|
| Residual Soil water content (PWP) | $\theta_r$ [-] | 0.15 | 0.15 |
| Saturated Soil Water Content (Porosity) | $\theta_s$ [-] | 0.50 | 0.50 |
| Saturated hydraulic conductivity | $K_s$ [cm d$^{-1}$] | 54 | 54 |
| Clapp and Hornberger Parameters | $b$ | 4.50 | |
| | $\psi_s$ | -7.80 | |
| | $W_i$ | 0.92 | |
| | $\psi_i = y$ | -11.35 | |
| | $m=m1$ | -1079.61 | |
| | $n=m2$ | 0.78 | |
| Averjanov (empirical n factor) | $n$ | | 6 |

***Table 4.5***. Soil moisture and soil temperature and N dynamics were calculated on a daily time step with a 30 minutes temporal discretization. The lower boundary in the model was a free draining layer, while the upper layer was the open atmosphere. Water entered the profile mainly through precipitation as no irrigation water was applied and the slope was less than 5° so that no overland flow or runoff was considered. The significant processes through which water was removed from the model were by evapotranspiration to the atmosphere and by free drainage beyond plant root. All precipitation in infiltrated into the soil in the model and the soil was drained to field capacity within 24 hours by cascade approach (Li et al. 1992; Smith et al. 2020).

**Table 4.3** Farm management operations on the study site at Carman.

| | | **Year** | | | |
|---|---|---|---|---|---|
| | **Farm operation** | **2011** | **2012** | **2013** | **2014** |
| **Annual plot** | Crop | Canola | Barley | Canola | Barley |
| | Tillage | 17 June | 15 May | 11 June | 6 June |
| | Manure application | 17 June | 15 May | 11 June | 6 June |
| | Planting/seeding | 17 June | 15 May | 11 June | 6 June |
| | Harvest | 20 September | 21 August | 6 September | 27 August |
| **Perennial forage** | Crop | Timothy/ Orchard | Timothy/ Orchard | Canola | Timothy/ Orchard |

| | | | | |
|---|---|---|---|---|
| Tillage | - | - | 11 June | - |
| Manure application | | | 11 June | |
| Planting/seeding | - | - | 11 June | |
| First cut | 6 July | | 6 September | |
| Second cut | 29 August | | - | |

### 4.3.6 Model Calibration

Model calibration is a process that involves changing model input parameters, running the model, and adjusting the parameter after assessing the result until a good fit is observed. The target parameters for calibration in this model were soil moisture and $N_2O$ flux. The following input parameters were used to calibrate the model and observed for how they affect the model result: hydraulic conductivity, total porosity, field capacity, permanent wilting point, soil organic matter content, clay fraction, bulk density, biomass C:N ratio, N fixation index, crop water demand, and maximum yield. The model was manually calibrated using the trial and error approach starting with field measured values and model defaults and the goodness of fit was evaluated with the evaluation criteria. The control plots CON was used to calibrate the model. I ran the model for a period of 14 years consisting of 10 years model warm-up period to get the model to a steady-state, and 4 years that coincided with our experimental period from 2011-2014. I chose a period of 10 years for the spin-up period because a more extended period did not influence the result significantly. Uzoma et al. (2015) successfully used ten years spin up period and made success with it.

### 4.3.7 Model Validation

The LPM and SPM treatments on both ANN and FER plots were individually used to validate the model. The validation model equally spun up for a period of 10 years to allow for steady state. Soil moisture (0-10 cm) and $N_2O$ flux data from 2011 to 2014 were used for data validation in each of the treatment plots. The model calculated values and field observed values were compared using the evaluation criteria $R^2$, RMSE, NRMSE, ME and NSE

### 4.3.8 Sensitivity analysis

Sensitivity analysis can be carried out by varying the model parameters to observe how the model result responded to variations in the input parameter (Holländer et al. 2015; Singh et al. 2019). Soil moisture and cumulative $N_2O$ flux were the major output parameters considered in the model sensitivity analysis as the calibration showed less variation in soil temperature resulting from changes in input values. Also, only control treatments of annual plots (CON ANN) were considered for the sensitivity analysis as the same trend applies to the rest of the treatments. All tested input variables were varied at ±1%, ±5%, ±10%, ±25% and ±50%. The relative sensitivity index was used to assess the impact of the input parameters on the output of the model with a higher value indicating greater impact (Deng et al. 2016; Li et al. 2014).

$$S = \frac{\left(\frac{O_{max} - O_{min}}{O_{mean}}\right)}{\left(\frac{I_{max} - I_{min}}{I_{mean}}\right)} \qquad (16)$$

Where $S$ = relative sensitivity index, $I_{max}$ = maximum input value tested, $I_{min}$ = minimum input value tested, $I_{mean}$ = mean of *input values tested*, $O_{max}$ = modelled output value corresponding to $I_{max}$, $O_{min}$ = modelled output value corresponding to $I_{min}$, $O_{mean}$ = mean of *output values from inputs tested.*

### 4.3.9 Statistics and Model Evaluation

The goodness of fit between the modelled and field observed soil moisture and $N_2O$ flux data was carried out using the following statistical parameters: Coefficient of determination ($R^2$), Root Mean Square Error (RMSE), Normalized Root Mean Square Error (NRMSE), Mean Error (ME), and Nash-Sutcliffe Model Efficiency (NSE).

#### 4.3.9.1 Coefficient of Determination ($R^2$), 0 to +1

$R^2$ has a range of 0 to 1, the closer to 1 the better is the fit between the modelled and measured data. It is a measure of goodness of fit that shows the proportion of the variation in the outcome that can be explained by the model.

$$R^2 = \left( \frac{\sum_{i=1}^{n}(O_i - \bar{O}) \times (C_i - \bar{C})}{\sqrt{\sum_{i=1}^{n}(O_i - \bar{O}_i)^2 \times \sum_{i=1}^{n}(C_i - \bar{C}_i)^2}} \right)^2 \tag{14}$$

Where O = Field observed values, C= Model calculated values, n = Number of observations

$\bar{O}$ = Mean of observed data, $\bar{C}$ = Mean of calculated data, i = iteration count

#### 4.3.9.2 Root Mean Square Error (RMSE), *scale-dependent*

The RMSE aggregates the residual errors into a standard measure of goodness of fit. It measures the standard deviation of the difference between the modelled and observed data.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(O_i - C_i)^2}{n}} \tag{15}$$

#### 4.3.9.3 Normalized Root Mean Square Error (NRMSE), 0 to 100

The normalized root mean square relates the RMSE to the observed range or mean observed variables allows for comparison of model at different scales.

$$NRMSE = \frac{RMSE}{\bar{O}} \times 100 \tag{16}$$

#### 4.3.9.3 Nash-Sutcliffe Model Efficiency (NSE)

$$NSE = 1 - \frac{\sum_{i=1}^{n}(O_i - C_i)^2}{\sum_{i=1}^{n}(O_i - \bar{O})^2} \tag{17}$$

The NSE has a range from -∞ to +1, a value less than zero means that the observed mean is a better predictor than the model estimates, a value of zero means that the observed mean is as equal as the model estimate in predicting the outcome, values greater than zero indicate that the model is a better predictor than the observed mean, while a value of one indicates the model is a perfect predictor of the outcome. For a better model performance, I strive to achieve an NSE greater than 0.5 (Moriasi et al. 2007).

#### 4.3.9.4 Mean Error (ME) *scale dependent*

$$ME = \frac{\sum_{i=1}^{n}(O_i - C_i)}{n} \qquad (18)$$

Where O = Field observed values, C= Model calculated values, n = Number of observations

$\bar{O}$ = Mean of observed data, $\bar{C}$ = Mean of calculated data, i = iteration count (Moriasi et al. 2007; Nash and Sutcliffe 1970).

## 4.4 Results and Discussion

### 4.4.1 Model calibration

The water retention curve and hydraulic conductivity function for the two approaches used in the DNDC vs. Clapp and Hornberger-Campbell and Averjanov and Irmay was compared (Figure 4.1) using data from optimizes soil parameter (Table 4.4 and Table 4.5). The curve revealed that water retention curve of Clapp and Hornberger and Averjanov and Irmay were similar, from saturation to field capacity (FC) to permanent wilting point (PWP). The hydraulic conductivity function was also similar. For both Campbell and Averjanov (Figure 4.1 b), the hydraulic conductivity at saturation matric potential was virtually the same as that at field capacity. The release of soil moisture in soil is not only a function of soil water content but the tension with which the water is held in soil.

The modelled soil moisture had a good fit with $R^2$ values of greater than 0.5 except on FPP plots (Figure 4.2; Figure 4.3; Figure 4.4). However, on the FPP plot, soil moisture was capped at 0.42 $cm^3$ $cm^{-3}$ WFPS, which falls within the range of field capacity specified in the model. (Figure 4.2and Figure 4.3);. Soil $N_2O$ flux was equally well captured by the model, most especially on a seasonal time scale.

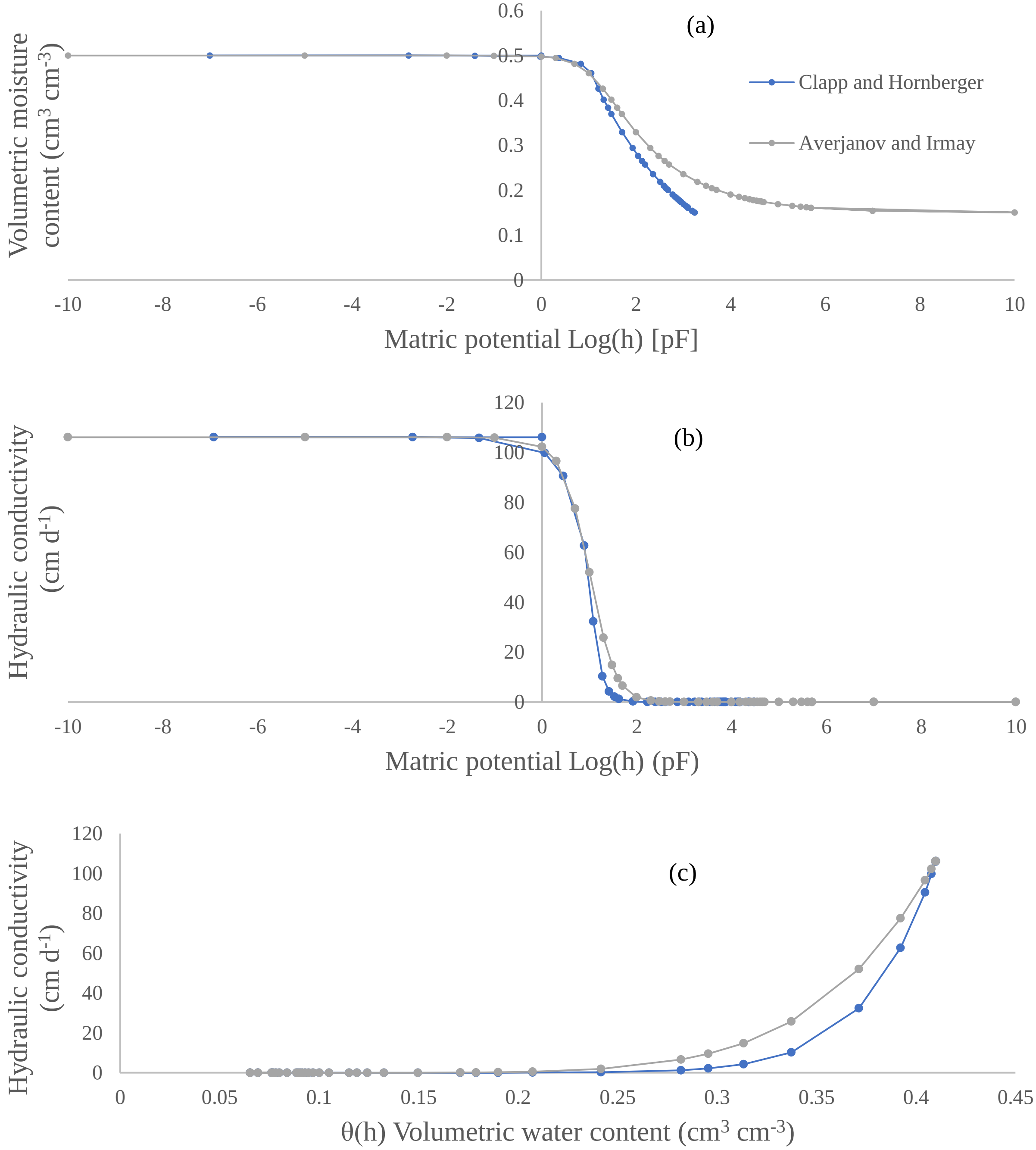

(a)
Volumetric moisture content (cm3 cm-3)
0.6
0.5
0.4
0.3
0.2
0.1
0
-10 -8 -6 -4 -2 0 2 4 6 8 10
Matric potential Log(h) [pF]
Clapp and Hornberger
Averjanov and Irmay
(b)
Hydraulic conductivity (cm d-1)
120
100
80
60
40
20
0
-10 -8 -6 -4 -2 0 2 4 6 8 10
Matric potential Log(h) (pF)
(c)
Hydraulic conductivity (cm d-1)
120
100
80
60
40
20
0
0 0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4 0.45
θ(h) Volumetric water content (cm3 cm-3)

**Table 4.4** Optimized soil parameters used in plotting retention curve and hydraulic conductivity function for soil depth 0 - 10 cm.

| Description | Soil Parameters | Clapp and Hornberger | Averjanov and Irmay |
|---|---|---|---|
| Residual Soil water content (PWP) | $\theta_r$ [-] | 0.15 | 0.15 |
| Saturated Soil Water Content (Porosity) | $\theta_s$ [-] | 0.50 | 0.50 |
| Saturated hydraulic conductivity | $K_s$ [cm $d^{-1}$] | 54 | 54 |
| Clapp and Hornberger Parameters | $b$ | 4.50 | |
| | $\psi_s$ | -7.80 | |
| | $W_i$ | 0.92 | |
| | $\psi_i = y$ | -11.35 | |
| | $m=m1$ | -1079.61 | |
| | $n=m2$ | 0.78 | |
| Averjanov (empirical n factor) | $n$ | | 6 |

**Table 4.5** Final calibration parameters used in calibrating DNDC v.Can and DNDC 9.5.

| **Category** | **Input Parameters** | **Layer 1*** | **Layer 2** | **Layer 3** | **Unit** |
|---|---|---|---|---|---|
| Soil properties | Thickness | 0.15 | 0.3 | 1.55 | m |
| | Texture | Sandy loam | Loam | Sandy clay | |
| | Clay fraction | 0.09 | 0.19 | 0.43 | |
| | Bulk density | 1.23 | 1.45 | 1.5 | g $cm^{-3}$ |
| | Soil pH | 6.79 | 7.8 | 9 | |
| | Field capacity (WFPS) | 0.42 | 0.60 | 0.70 | $cm^3$ $cm^{-3}$ |
| | Wilting point (WFPS) | 0.15 | 0.22 | 0.28 | $cm^3$ $cm^{-3}$ |
| | Hydraulic conductivity | 0.0225 | 0.012 | 0.008 | m/hr |
| | Porosity (0-1) | 0.5 | 0.45 | 0.43 | |
| | SOC at surface (0-10 cm) | 0.028 | 0.025 | 0.01 | kg C $kg^{-1}$ soil |
| N Processes | Denitrifier growth rate (0 - 2) | 0.7 | | | |
| | Nitrifier growth rate (0 - 2) | 1.2 | | | |
| | Nitrification factor (0 - 2) | 0.2 | | | |
| Crop Parameters | | Canola | Barley | | Non-leguminous hay |
| | Biomass fraction (grain/leaf/stem/root) | 0.23/0.28/0.28/0.21 | 0.38/0.24/0.24/0.15 | | 0.01/0.30/0.30/0.40 |
| | Biomass C:N ratio (grain/leaf/stem/root) | 13/55/55/45 | 25/75/75/85 | | 45/80/80/90 |
| | Annual N demand (kg N $ha^{-1}$ $yr^{-1}$) | 283 | 153 | | 120 |
| | Thermal degree day for maturity | 1600 | 1500 | | 2200 |
| | Water demand (g water $g^{-1}$ DM) | 85 | 85 | | 200 |

* The same calibration parameters were used for both DNDC 9.5 and DNDC v.Can except that only one layer was specified for DNDC 9.5 and N processes were not calibrated for DNDC 9.5 as there is no user interface to input these parameters.

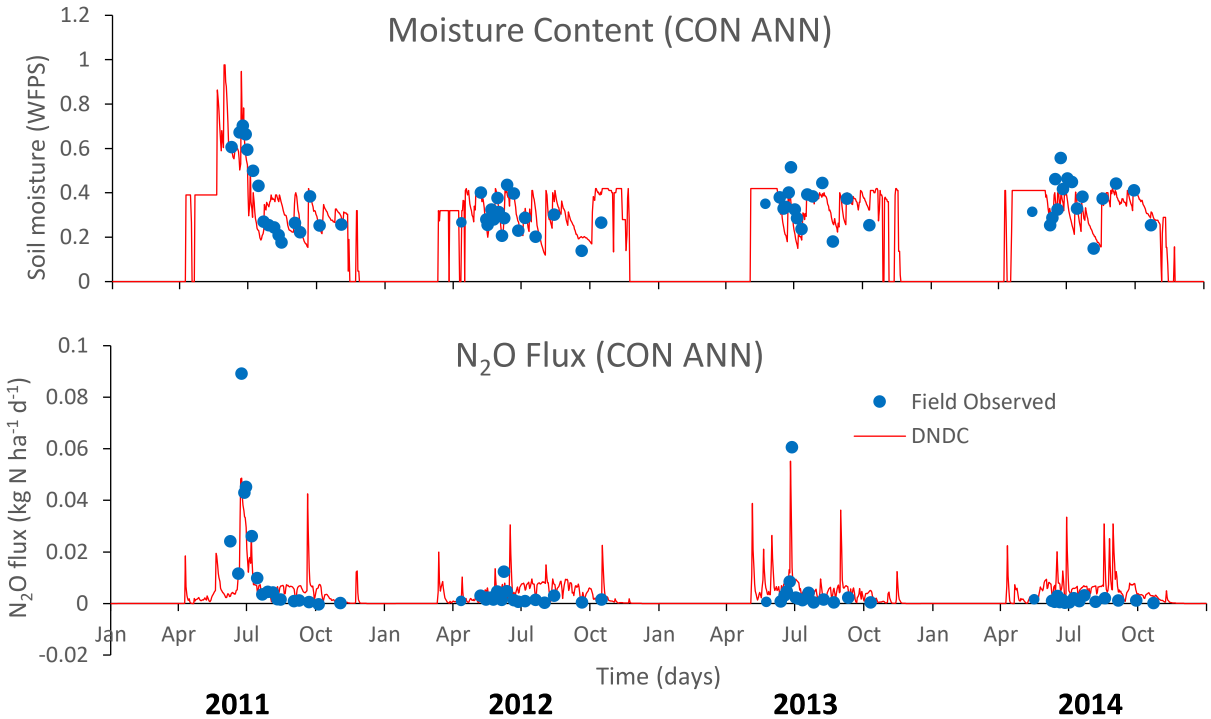



**Figure 4.2** Calibration result showing plot of field observed (dotted blue) and DNDC v.Can simulated (solid red line) values for soil moisture, and $N_2O$ flux on control (CON) plots of regular annual crop (ANN)

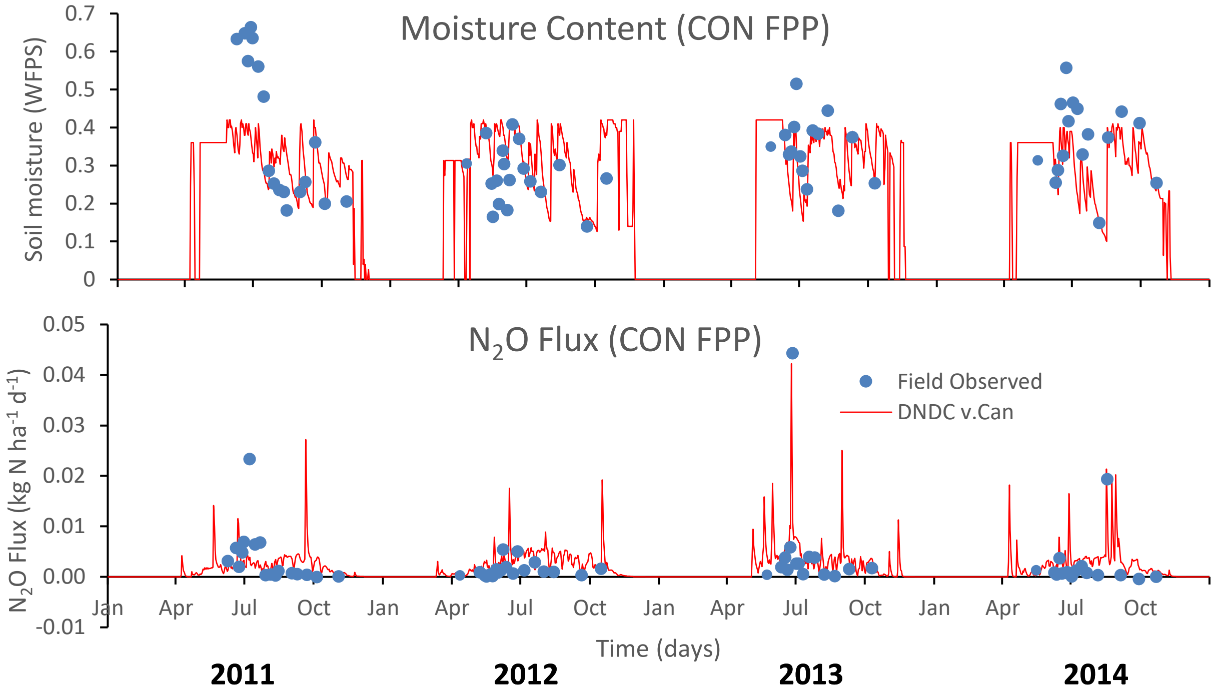



**Figure 4.3** Calibration result showing plot of field observed (dotted blue) and DNDC v.Can simulated (solid red line) values for soil moisture, and $N_2O$ flux on control (CON) plots of perennial forage grasses (FPP)

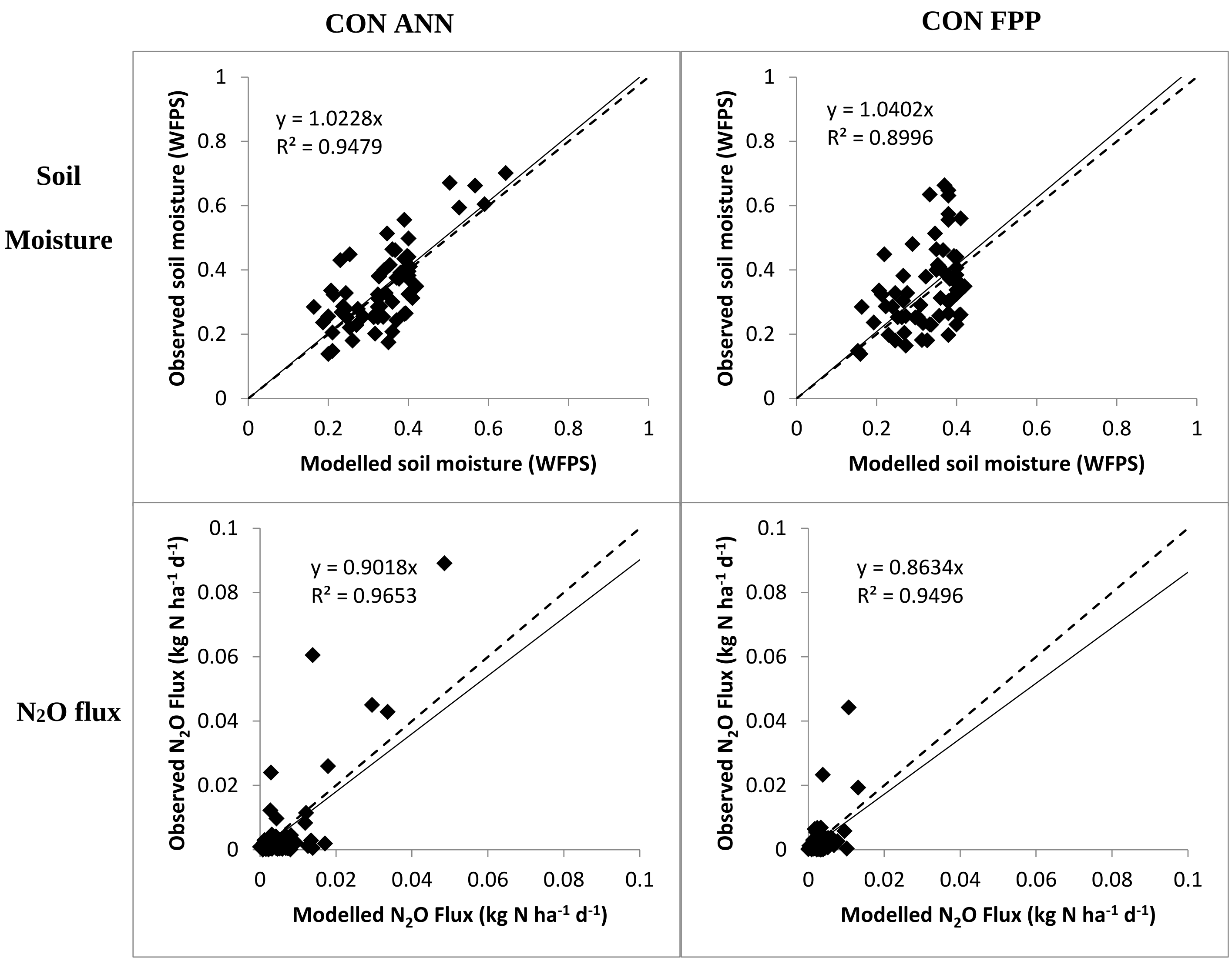
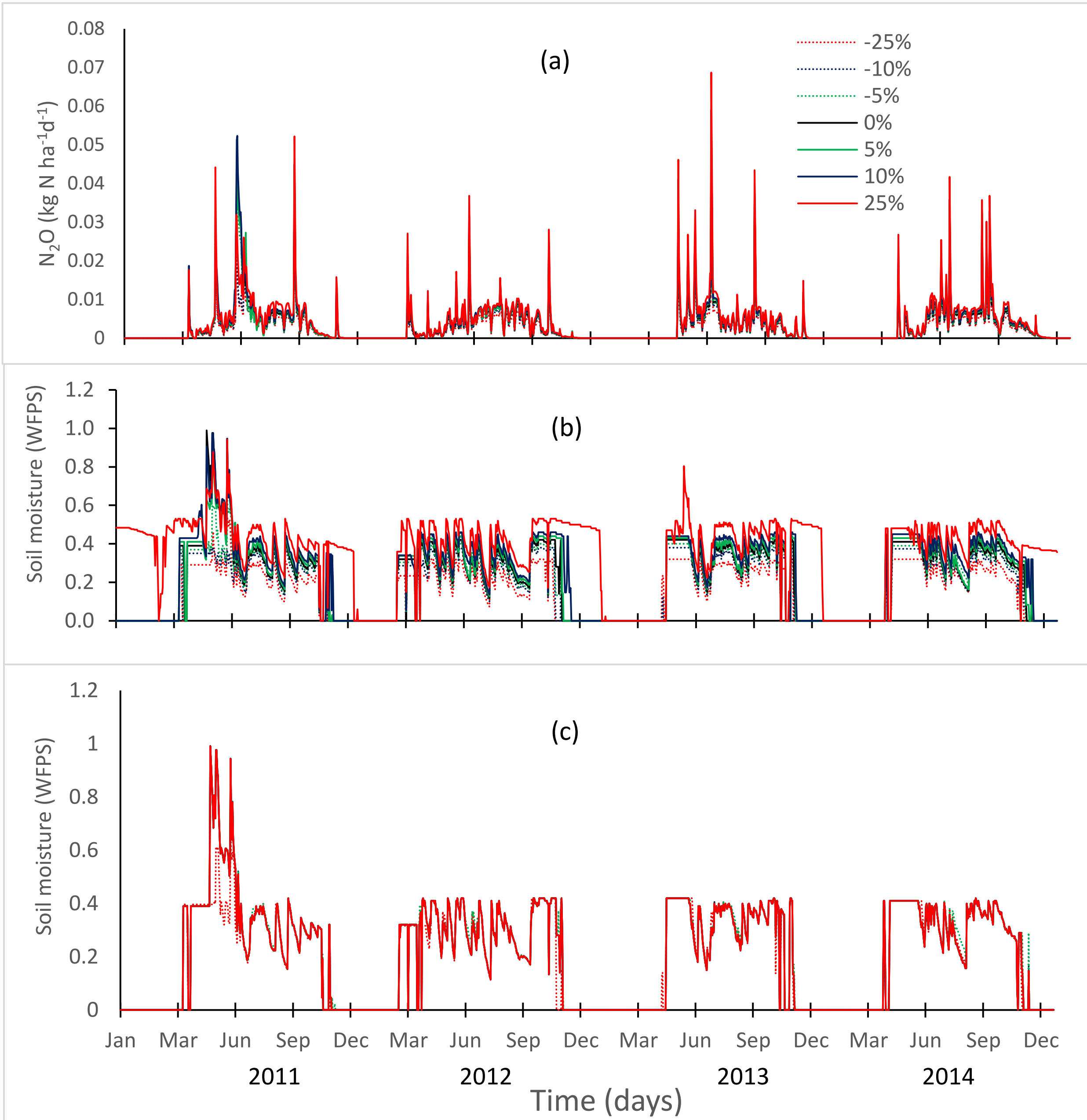



**Figure 4.4** Graph of field observed (soil moisture, and $N_2O$ flux) against DNDC modelled values on CON ANN and CON FPP from 2011 to 2014. The solid line represents the trend line of modelled vs observed values, while dashed lines indicate a perfect diagonal line for 1:1 comparison. Note that the $R^2$ here is adjusted to the intercept of zero

### 4.4.2 Sensitivity Analysis

The sensitivity plot (Figure 4.5) and the sensitivity index show that soil moisture was mostly affected by field capacity. On the control plots of annual treatment, I recorded a sensitivity index of 1.73, which equates to a 150 % change in the output of soil moisture when input values of field capacity were changed by 50%. Saggar et al. (2007) had reported similar observation that soil moisture (WFPS) from the DNDC model was highly sensitive to values of field capacity and permanent wilting point specified in the model. Hydraulic conductivity has less effect on the model result; the output soil moisture stood constant for variations in the input parameter with a sensitivity index of 0.04, which is low compared to that of the field capacity. A 50% change in hydraulic conductivity input resulted in barely any change in soil moisture output. Although this magnitude of change is so small such that field conditions are more variable. Sometimes, low sensitivity is desirable as it shows the model is robust and less likely to fluctuate due to minimal changes input parameter. $N_2O$ flux was moderately sensitive to changes in soil organic carbon content in the model with a sensitivity index of 1. A unit change in soil organic carbon content corresponds to approximately unit change in $N_2O$ flux. This is understandable as soil organic matter content is a measure of stored nitrogen in the soil.



(a)
(b)
(c)
N2O (kg N ha-1d-1)
Soil moisture (WFPS)
-25%
-10%
-5%
0%
5%
10%
25%
Jan
Mar
Jun
Sep
Dec
2011
2012
2013
2014
Time (days)

### 4.4.3 Comparison between DNDC v.Can and DNDC 9.5

I compared the result of the modified DNDC v.Can model with the original DNDC 9.5 to observe the differences between modelled values (Table 4.6). The result showed that the modified DNDC v.Can performed better than the original DNDC 9.5 in simulating soil moisture and $N_2O$ fluxes from crop and manure management. The NSE values of soil moisture and $N_2O$ flux on the DNDC 9.5 were mostly negative, which suggests that the observed mean was a better predictor than the model mean. On the other hand, DNDC v.Can showed positive NSE values, which shows that the model is a better predictor than the observed means (Table 4.6). Equally, the ME and RMSE values on DNDC v.Can are lower than that of DNDC 9.5. Thus, DNDC v.Can performed significantly better than DNDC 9.5 in this study.

**Table 4.6** Evaluation of observed and modelled soil moisture and $N_2O$ flux on control (CON) plots of regular annual (ANN) and perennial forage (FPP) plots.

| | | $R^2$ | | RMSE | | NRMSE | | ME | | NSE | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Parameter | DNDC v.Can | DNDC 9.5 | DNDC v.Can | DNDC 9.5 | DNDC v.Can | DNDC 9.5 | DNDC v.Can | DNDC 9.5 | DNDC v.Can | DNDC 9.5 |
| CON ANN | $N_2O$ flux | 0.67 | 0.08 | 0.010 | 0.016 | 154.31 | 247.63 | 0.001 | 0.005 | 0.58 | -0.09 |
| | Soil Moisture | 0.57 | 0.25 | 0.085 | 0.123 | 24.92 | 35.88 | -0.007 | -0.034 | 0.57 | 0.11 |
| CON FPP | $N_2O$ flux | 0.24 | 0.03 | 0.006 | 0.007 | 191.11 | 227.93 | 0.001 | -0.002 | 0.22 | -0.10 |
| | Soil Moisture | 0.23 | 0.05 | 0.117 | 0.186 | 34.71 | 55.14 | -0.015 | -0.115 | 0.22 | -0.98 |

### 4.4.4 Soil Moisture

The model performed better in modelling soil moisture from the annual plots with NSE ranging from 0.6 to 0.7 compared to the perennial plots with NSE values ranging from -0.1 to 0.2 (Figure 4.6, Table 4.7). Average daily growing season soil moisture WFPS up to 10 cm soil depth estimated from the study site ranged from 0.14 to 0.56 $cm^3$ $cm^{-3}$. Although the mean errors were low <0.05 $cm^3$ $cm^{-3}$, the NRMSE was considered fair, ranging from 20 to 30 %. These values were within the range reported in previous studies (He et al. 2019; Smith et al. 2020). Some lags were observed between modelled and observed daily soil moisture contents. There were several factors that caused the difference between the modelled and the field observed soil moisture contents.

First, is the fast drainage to field capacity. The field capacity and permanent wilting point defines the limit of water available to plant Figure 4.1 (a). The plant can take up water from the soil based on crop water demand from the available water content in the soil. Uzoma et al. (2015) noted already the inability of the DNDC model to simulate moisture content above field capacity, most especially during periods of episodic rainfalls irrigation or snow thaw events that saturate the soil over a long period. These occasions where soil moisture content is above 60 % WFPS are important because this is when denitrification abounds, and the denitrification routine is activated in the DNDC model (Li et al. 1992). But dues to the cascade approach used in the DNDC model, soil moisture drains quickly to field capacity than it would do under gravity in the field, thus soil moisture rarely goes above field capacity in the model.

Second, is the soil hydraulic conductivity. The hydraulic conductivity measured on the field would be different from that computed by the model. Although, models are not exact replication of field condition but a means to estimate important variable that will guide informed decisions. The model sensitivity in this study showed less variation in soil moisture output resulting from changes in hydraulic conductivity. This is because the input variation of 25 % change in hydraulic conductivity was small as to expect significant change in model output, because higher level of variations exists on the field from one spot to another. Different types of crops and nutrient management would have effect on soil hydraulic conductivity. Adesanya et al. (2016) reported that hydraulic conductivity from FPP was significantly higher than ANN, also hydraulic conductivity from SPM was significantly higher than LPM when managed over a five-year period. In this study, I calibrated the model for the best saturated hydraulic conductivity. Although the DNDC v.Can showed significant improvement over the DNDC 9.5 in estimating soil water from this study by using the Averjanov and Irmay retention curve, a look at Figure 4.1 (b) showed that more can still be achieved by using Mualem (1976) hydraulic conductivity function in place of Averjanov (1950) or Campbel (1974).

Third, is the cascade approach of estimating soil water flow in the DNDC model. The recent introduction of heterogenous layer has improved the simulation performance of DNDC v.Can over DNDC 9.5 but the model still kept the cascade approach due to its simplicity. Smith et al. 2020 reported a 4 times fast performance compared to equivalent Root Zone Water Quality Model 2 (RZWQM2) that employs detailed computational processes in estimating soil water content. Also, not a lot of variables are required to estimate moisture content using the cascade approach. Even with the current implementation of heterogenous layer that allows for variable soil properties, the DNDC v.Can does to provide an interface for discretization within layers. To improve soil moisture content estimation from the DNDC model I suggest an implementation of a robust computational approach using continuity equation as that of Richard's. The model should allow for variable discretization of temporal and spatial domain for refined processes.

Lastly is the crop water uptake capability of perennial forage grasses compared to annual crops. Perennial forage grasses have fibrous roots which differs from regular annual crops, consequently difference in water uptake from soil. Lasisi et al. (2018) reported that FPP roots are 5 times greater than that from ANN which eventually affected soil water uptake. Although, I calibrated the model for crop water uptake, which is different for both annual crops and perennial forage grasses (Table 4.4 *Optimized soil parameters used in plotting retention curve and hydraulic conductivity function for soil depth 0 - 10 cm.*

| **Description** | **Soil Parameters** | **Clapp and Hornberger** | **Averjanov and Irmay** |
|---|---|---|---|
| Residual Soil water content (PWP) | $\theta_r$ [-] | 0.15 | 0.15 |
| Saturated Soil Water Content (Porosity) | $\theta_s$ [-] | 0.50 | 0.50 |
| Saturated hydraulic conductivity | $K_s$ [cm d$^{-1}$] | 54 | 54 |
| Clapp and Hornberger Parameters | $b$ | 4.50 | |
| | $\psi_s$ | -7.80 | |
| | $W_i$ | 0.92 | |
| | $\psi_i = y$ | -11.35 | |
| | $m=m1$ | -1079.61 | |
| | $n=m2$ | 0.78 | |
| Averjanov (empirical n factor) | $n$ | | 6 |

***Table 4.5***). The model result showed a better performance for annual crops compared to perennial forage grasses Figure 4.6. The last crop growth performance implemented in the DNDC v.Can model was carried out using spring wheat by Kröbel (2011). A new growth function for perrennial forage grasses that will account for large root biomass which varies with above ground biomass would help to improve the water uptake in the model.

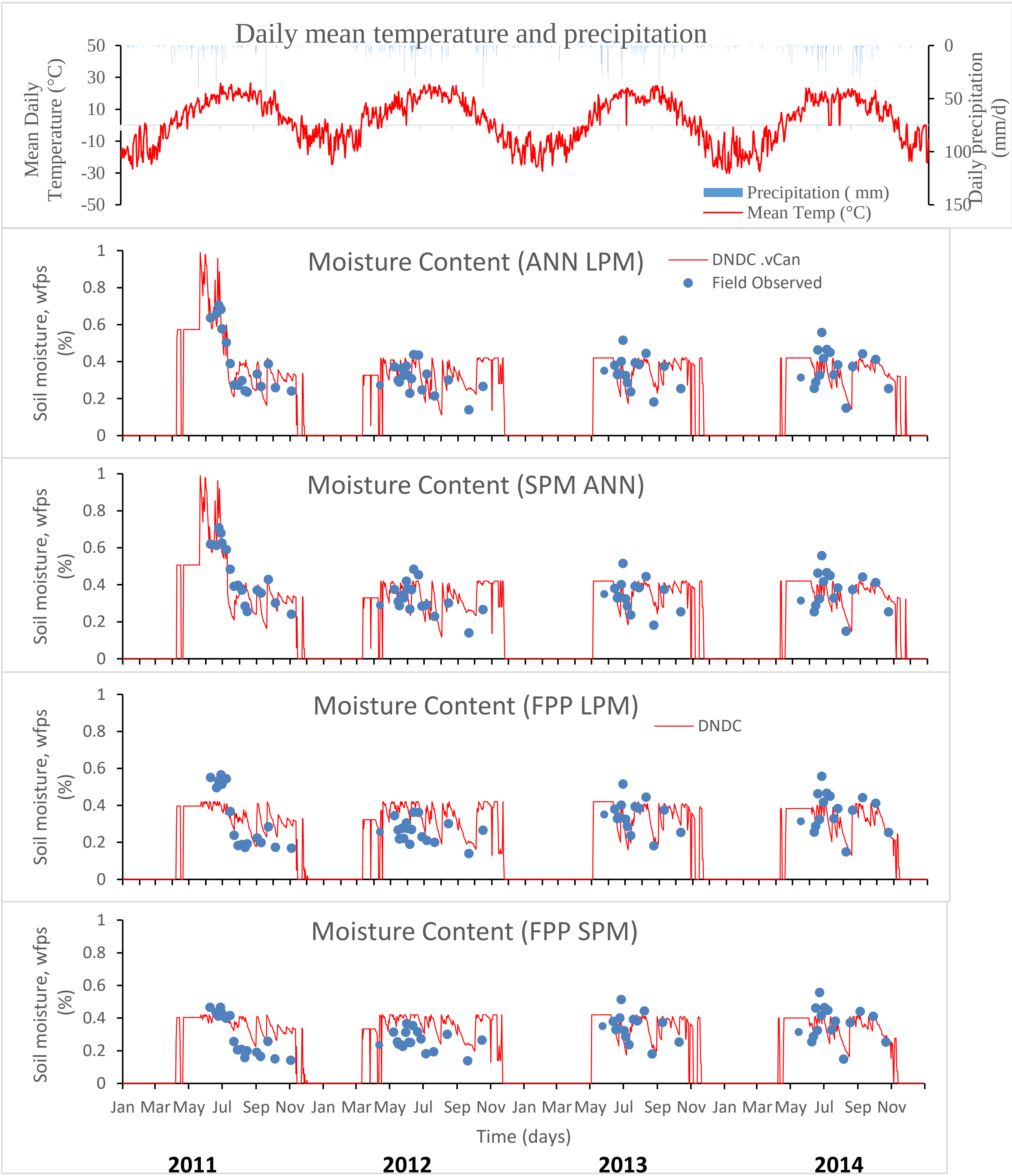

Daily mean temperature and precipitation
Mean Daily Temperature (°C)
Daily precipitation (mm/d)
Precipitation ( mm)
Mean Temp (°C)
Moisture Content (ANN LPM)
DNDC .vCan
Field Observed
Moisture Content (SPM ANN)
Moisture Content (FPP LPM)
DNDC
Moisture Content (FPP SPM)
Soil moisture, wfps (%)
Time (days)
2011
2012
2013
2014

**Table 4.7** Comparison of model-simulated and field observed average daily soil moisture content values on perennial forage grasses (FPP) and annual crops (ANN) amended with liquid pig manure (LPM) and solid pig manure (SPM) from 2011 to 2014.

| **Cropping System** | **Manure Treatment** | **$R^2$** | **NSE** | **NRMSE** | **RMSE** | **ME** | **DNDC v.Can** | **Field Observed** |
|---|---|---|---|---|---|---|---|---|
| | | | | **(%)** | **--------------- ($cm^3$ $cm^{-3}$) --------------------** | | | |
| ANN | LPM | 0.67 | 0.7 | 20.9 | 0.07 | 0.009 | 0.36 | 0.35 |
| ANN | SPM | 0.63 | 0.6 | 21.05 | 0.08 | <0.001 | 0.37 | 0.37 |
| FPP | LPM | 0.25 | 0.2 | 33.6 | 0.11 | 0.024 | 0.34 | 0.32 |
| FPP | SPM | 0.2 | -0.1 | 36.3 | 0.11 | 0.052 | 0.36 | 0.31 |

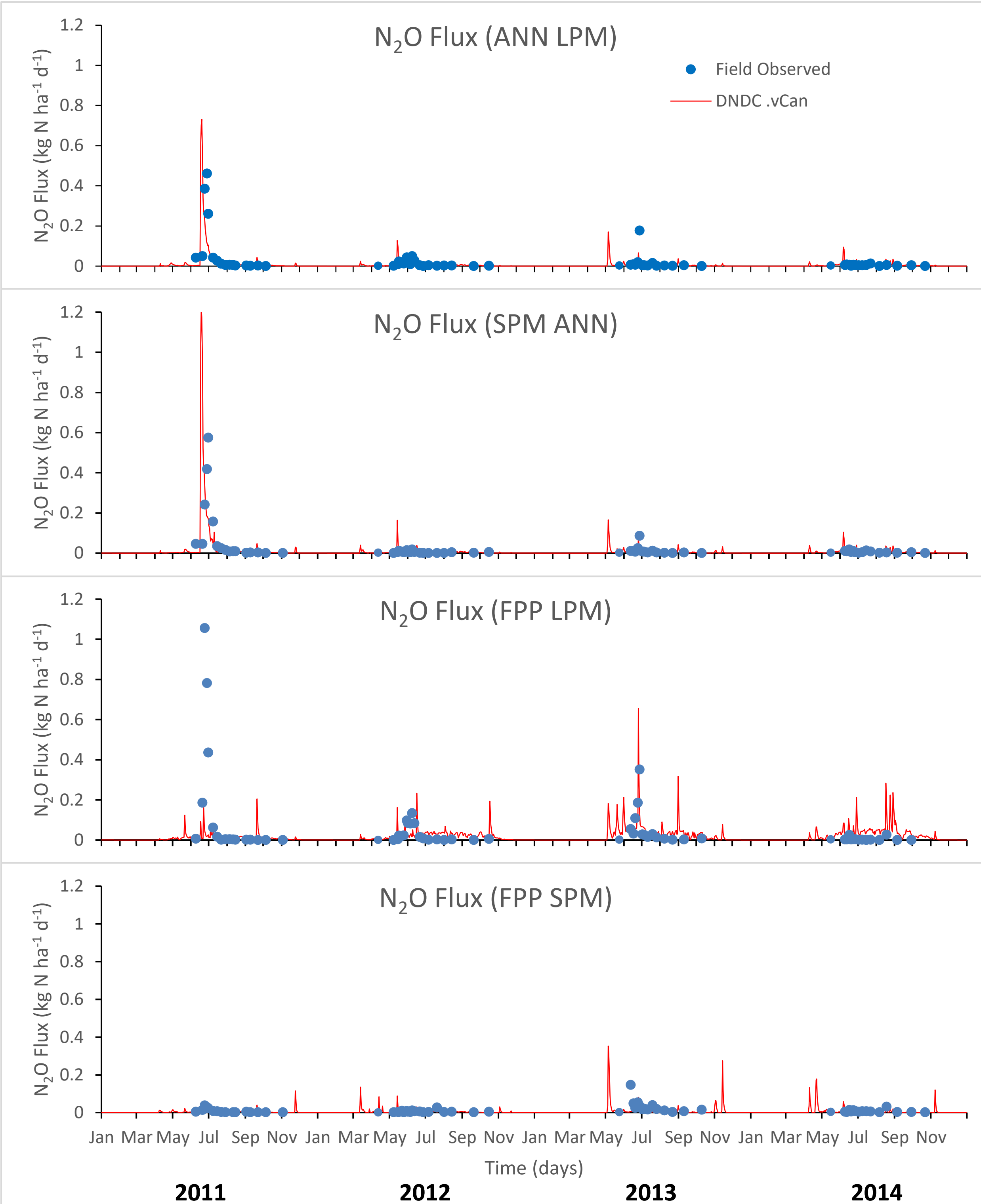
### 4.4.5 $N_2O$ Flux

During the 4-year growing season, cumulative $N_2O$ flux modeled with DNDC v.Can ranged from 3 to 22 kg N $ha^{-1}$ as compared with field measured values of 4 to 17 kg N $ha^{-1}$ respectively (Table 4.8). These values from the model were comparable to the field observations most especially on the ANN plots, with NRMSE values ranging from 20 to 30 % on the ANN plots (Table 4.8). Over the entire 4-year simulation period, the model revealed that SPM of FPP had the least cumulative $N_2O$ flux (2.8 kg N $ha^{-1}$) over one growing season among the treatments considered as compared to the highest flux from LPM of FPP (21.7 kg N $ha^{-1}$). This also corresponds to the cumulative measured values from the field on SPM FPP (4.2 kg N $ha^{-1}$) and LPM FPP (17.3 kg N $ha^{-1}$), respectively (Table 4.8). Although the model appears to underestimate $N_2O$ flux from SPM FPP (Figure 4.7), I attribute the difference between measured and simulated values to inability of the DNDC to effectively model soil nitrate and ammonium in the soil (data not shown). Although the model appeared to underestimate $N_2O$ flux from LPM on FPP in 2011, it was able to capture the perennial forage plow down on the treatment in 2013 (Figure 4.7). From 2009 to 2012, the FPP plots had been in managed grassland receiving an annual application of pig manure. In the fall of 2012, the FPP was terminated and plowed in; this resulted in a high flux of $N_2O$ following cultivation and manure application in the following year (Adelekun et al. 2019).

The model performed better in estimating cumulative growing season $N_2O$ fluxes from regular annual plots (ANN) than perennial forage plots (FPP) with NSE values of 0.9 and -0.5, respectively (Table 4.8). Similarly, the NRMSE from cumulative growing season $N_2O$ emissions also showed a value of 18% and 31% on SPM and LPM of ANN, respectively, as compared 99% and 112% on SPM and LPM respectively of FPP (Table 4.8). Various factors could have influenced this disparity, which includes i) soil moisture ii) crop root distribution iii) tillage and iv) applied manure

N. The inability of DNDC to effectively simulate soil moisture from managed grassland (Table 4.7) affected the modelled $N_2O$ flux from the treatments. Due to the extensive fibrous root nature of the FPP, the rate at which it absorbs and utilise soil moisture will be different compared to ANN. Lasisi et al. (2018) reported that the root biomass from FPP receiving the annual application of manure was more than five times greater than that of ANN, and consequently, N uptake by FPP was equally five times greater than that of ANN. Forage grasses can store more N from the soil as compared to ANN because of their rooting density. I identify that the crop growth function of forage grasses in the DNDC v.Can be revaluated to include dynamic root biomass that depends on crop type and growth stages. He et al. (2020) has also reported on the need to incorporate below-ground biomass function to capture soil water and N uptake from FPP. In the course of calibration, I observed that for tillage, because the FPP plot was not tilled during the growth of the perennial forage grasses, the model underestimated $N_2O$ flux from the FPP during this period when manure was applied to the soil without tillage compared to ANN that was tilled (data not shown). It is important to identify that $N_2O$ fluxes are more prevalent with timing of N application. The amount of N applied and the form in which the N is applied also have significant effects on $N_2O$ flux. As observed in the calibrations section, the model underestimated soil nitrate from the manure applications, which was even more pronounced in the FPP plots (Figure 4.2). He et al. (2020) also identified similar observation that the DNDC v.Can model underestimated soil $NO_3^-$-N from their forage plots. Partitioning manure content into various form of N it can supply and accurate release of this components as at when needed in the soil could help improve $N_2O$ estimation in the DNDC model.

Another major observation was that the model performed better in estimating cumulative seasonal $N_2O$ flux compared to daily average values. This is understandable, as the model was originally developed to capture seasonal cumulative $N_2O$ emission rather than daily flux (Li et al. 1992). Also, several studies have previously noted the limitation of the DNDC in accurate estimation of daily $N_2O$ flux (He et al. 2019; Uzoma et al. 2015; Smith et al. 2019). Giltrap et al. (2015) and He et al. (2019) mentioned several factors that could have influenced the accurate estimation of daily $N_2O$ flux from the model which include, inaccurate estimation of soil moisture, underestimation of soil inorganic nitrogen, soil microbial activities, soil nitrate leaching and ammonia volatilization. As described under the moisture section above, better processing of the soil water flow will improve $N_2O$ estimation in the model. The N dynamics in the model would need to be re-evaluated for accurate estimation of $N_2O$ emissions.



N2O Flux (ANN LPM)
Field Observed
DNDC .vCan
N2O Flux (SPM ANN)
N2O Flux (FPP LPM)
N2O Flux (FPP SPM)
N2O Flux (kg N ha-1 d-1)
1.2
1
0.8
0.6
0.4
0.2
0
Jan Mar May Jul Sep Nov Jan Mar May Jul Sep Nov Jan Mar May Jul Sep Nov Jan Mar May Jul Sep Nov
Time (days)
2011
2012
2013
2014

**Table 4.8** Comparison of model-simulated and field observed growing season cumulative and average daily $N_2O$ flux values on perennial forage grasses (FPP) and annual crops (ANN) amended with liquid pig manure (LPM) and solid pig manure (SPM) from 2011 to 2014.

| Cropping System | Manure Treatment | $R^2$ | NSE | NRMSE | RMSE | ME | DNDC v.Can | Field Observed |
|---|---|---|---|---|---|---|---|---|
| **4-Year growing season cumulative $N_2O$ flux** | | | | **(%)** | **----------------- (kg N $ha^{-1}$) ----------------** | | | |
| ANN | LPM | 0.97 | 0.96 | 20.10 | 0.427 | 0.057 | 8.50 | 8.00 |
| ANN | SPM | 0.99 | 0.96 | 23.60 | 0.592 | 0.400 | 12.00 | 10.00 |
| FPP | LPM | 0.72 | -1.10 | 130.13 | 5.628 | -1.106 | 21.73 | 17.30 |
| FPP | SPM | 0.01 | -0.21 | 77.44 | 0.805 | 0.346 | 2.78 | 4.16 |
| **Average daily $N_2O$ flux** | | | | **(%)** | **----------------- (kg N $ha^{-1}$ $d^{-1}$) ----------------** | | | |
| ANN | LPM | 0.17 | -0.09 | 298.4 | 0.083 | -0.006 | 0.021 | 0.028 |
| ANN | SPM | 0.11 | -0.93 | 431.2 | 0.126 | 0.002 | 0.030 | 0.029 |
| FPP | LPM | 0.017 | -0.01 | 278.7 | 0.171 | -0.029 | 0.033 | 0.061 |
| FPP | SPM | 0.042 | -0.08 | 187.7 | 0.021 | -0.007 | 0.004 | 0.011 |

## 4.5 Conclusion

This study evaluated the DNDC v.Can model for soil moisture and $N_2O$ flux from on a soil amended with liquid and solid pig manure and cropped to perennial forage and annual crops. The sensitivity analysis of the model showed that water filled pore space in the model was most sensitive to field capacity with relative sensitivity index of 1.73 whereas the moisture content in the model was not sensitive to hydraulic conductivity (RSI = 0.04) even after varying the input parameter by values greater than 150%. This is because of the cascade approach used in the model which caps soil moisture at set field capacity, this renders the water retention and hydraulic conductivity function less efficient in the model. This approach affects water flow in soil and eventually impact the $N_2O$ flux. As such I suggest a more robust mechanism in determining water flow in the model. The addition of continuity equation such as that of Richard's in place of tipping bucket approach will likely improve the model output. Soil $N_2O$ flux was better simulated on the ANN plots compared to the FPP plot. This, I attributed to the ability of the DNDC model to accurately estimate moisture flow in the soil in combination with moisture and nutrient uptake by fibrous root systems such as FPP. Also, the model performed better in simulating seasonal cumulative $N_2O$ flux compared to daily flux. Overall, the model performed well in simulating soil moisture and nitrous oxide fluxes from this study and as such can be used to estimate the future effect of similar crop and manure management on greenhouse gas fluxes. That being said, more work is needed on the working system of the DNDC model as seen on the FPP plots.

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# 5. OVERALL SYNTHESIS

## 5.1 Important Research Findings and Implications

There has been an increase in manure production in the world owing to an increase in animal production to meet the demand of the growing human population (Grossi et al. 2019). Land application of manure is the best avenue to manage the large waste from pig farms, which can serve as an alternative nutrient to plant in place of inorganic fertilizers. A significant concern generally with nitrogen source application to plant is the loss of N to the environment in the form of $N_2O$. Not only the cost of purchasing the fertilizer or organic manure a concern but also of environmental concern as $N_2O$ is a powerful greenhouse gas which is also capable of depleting the ozone layer that protects our atmosphere. Thus, the need to manage the source and rate of N application to our soils. Planting perennial forage grasses are helpful in managing manure applied to cropped land (Karimi et al. 2017; Lasisi et al. 2018), but what happens to the stored nitrogen when perennial forage grasses are plowed down and converted to annual plots? This scenario was simulated to evaluate the performance of DNDC v.Can and see how management and environmental factors affect nitrous oxide flux from manured fields? In this thesis, I measured and modelled $N_2O$ fluxes from perennial forage grasses and annual crops amended with pig manure and inorganic fertilizer.

The thesis was divided into three studies. The first study focused on assessing the nitrous oxide implication of converting perennial forage grasses with an annual application of liquid and solid pig manure to annual crop. The second study compared $N_2O$ emission from liquid pig manure and inorganic fertilizer applied to annual crops. The third study modelled soil moisture and $N_2O$ fluxes from perennial forage and annual crops amended with liquid pig manure and solid pig manure using the Denitrification Decomposition (DNDC) model.

The connecting line between these studies is how crop and nutrient management practices affect nitrous oxide emission from the soil.

The result from this dissertation showed that the conversion of perennial forage grasses receiving an annual application of pig manure into annual plots resulted in high $N_2O$ emission. According to Nikiema et al. (2016), including FPP in rotation with annual crops will have N saving benefits and help to reduce $N_2O$ flux from agricultural soil. This study however, showed that part of N accumulated during the forage phase could be lost as $N_2O$ among other forms in the conversion phase if adequate consideration is not taken to account for the N that will be released from the terminated crop.

The result also showed that a significant amount of N in the form of nitrate was release from the soil following the plowed down of FPP which affected the $N_2O$ flux from the plots. The implication of this is that N credit must be given to the termination of non-leguminous forage grasses receiving an annual application of manure because the application of more manure N that does not take cognisance of terminated FPP will likely result in excess N than is required by the plant. The excess N may be lost to the environment as $N_2O$ flux or nitrate leaching.

In comparing nitrous oxide flux from LPM and FER, the result from chapter 3 of this thesis showed that cumulative $N_2O$ emission, emission factor and emission intensity were significantly less on LPM than FER in two out of the three years considered in this study. Manure dry matter, applied N content and environmental factor including precipitation were the major factors that affected $N_2O$ flux from the study. The N applied in manure affected the N that was available in soil and $N_2O$ emission to the atmosphere. The implication of this study is that source of N and the rate of applied N played an essential role in $N_2O$ emission from agricultural soils. Manure properties such as dry matter content, total N content and total ammonium content is a factor that determined the application rate of LPM in the second study at Carberry (Chapter 3). I ran a correlation of these manure properties with their respective cumulative $N_2O$ flux each year. I observed a strong positive correlation between these manure properties and $N_2O$, explaining up to 80% of the flux at Carberry, where N application rate was based on Manure volume. On the other hand, at Carman where N rate was based on crop requirement, the relationship was not sustained under extreme fluxes. This is because other factors influenced the $N_2O$ flux. This implies that manure properties will affect $N_2O$ flux when N is applied based on Constant volume of manure as is the case in the second study of this thesis at Carberry (Chapter 3) but may not be a significant factor if N is applied base on crop requirement (Chapter 2).

The results from modelling $N_2O$ flux from FPP and ANN receiving an annual application of pig manure followed a similar pattern as field observed data. The model was able to capture peak emissions from the plots, most especially in 2013, during the conversion phase on FPP. $N_2O$ flux was better simulated in ANN plots compared to FPP. It was observed that the model's ability to predict $N_2O$ flux was affected by soil moisture content estimated by the model. A few factors limit accurate estimation of soil moisture from the model which includes, the ability of the model to distribute soil water based on plant rooting system. The tipping bucket approach used in DNDC to estimate water flow limits the maximum water content to its field capacity. This implies that the model will not be able to differentiate episodic soil moisture events such as periods following heavy rainfall that saturates the soil. The implication from the simulation study is that the model can be used by policymakers and environmental protection agencies to estimate the amount of $N_2O$ flux following termination of FPP but more work is needed to make the model perform better prediction as seen on the FPP.

Overall, this thesis has explored the implication of converting FPP receiving an annual application of pig manure to ANN both by measurement and simulation. I equally explored the $N_2O$ implication of applying LPM and its equivalent available N rate applied as Urea to annual cropped land. I reported that soil N and $N_2O$ fluxes were greater on the terminated forage cropland that received an annual application of pig manure. I also reported and that that LPM had marginal crop yield advantage over FER. I reported that applied manure N, dry matter and carbon content were some of the factors that accounted for the differences in $N_2O$ emissions observed between LPM and FER apart from environmental factor. The results clearly suggest a $N_2O$ emission reduction benefit and a marginal crop yield advantage of LPM over FER. This implies that crop management, source and rate of N are important factors that will affect the loss of N to the environment in the form of $N_2O$ emission.

## 5.3 Recommendations

In chapter 2, the annual period following the conversion of perennial forage grasses only lasted one year before the reestablishment of the perennial forage grass. Allowing a longer period of annual cropping (e.g. 2-3 years) during the rotation will help one understand in greater detail the mineralization processes involved during the conversion phases. This will help to explain how residual soil N from the plow-down is used by the crop. Also in the chapter 2 study, manure was still been added after the plow-down which made it a little difficult to differentiate the $N_2O$ flux resulting from the forage termination and that of manure added. A separate study that looks at $N_2O$ flux from plowed down forage grasses and annual crop without addition of manure following the termination will help to explain the differences.

Chapter 3 described $N_2O$ flux from annual cropland amended with liquid pig manure and urea fertilizer. In the study LPM was applied annually at a rate of 56,000L $ha^{-1}$. As seen from the study, in 2013 when manure applied N was high, $N_2O$ flux was equally high compared to other years most especially when it coincided with high precipitation. Also, in 2012 when manure N was higher, the $N_2O$ flux increased drastically (Table S1, Table S3 and Figure S1). One may thus hypothesis that $N_2O$ flux increase exponentially with increase in applied manure N rather than just a linear relationship. This hypothesis is left to be tested. Future studies may also consider capturing ammonia volatilization during the LPM application, as that may help to explain part of the difference between $N_2O$ from LPM and FER.

Soil moisture is an important component in modelling greenhouse gas flux; more precise simulation of soil moisture content will yield a better result for greenhouse gas fluxes. Currently, the DNDC model uses the tipping bucket approach to simulate moisture flow across a soil profile. I suggest an implementation of more robust mathematical procedures such as the combination of Darcy flow with the continuity equation. In the course of running the calibration for the model in chapter 4, I did observe that soil available nitrogen including ammonium and nitrate were poorly predicted by the model (data not shown). I will recommend that this routine be revisited to provide more accurate estimation of soil N which is a prominent driving factor in $N_2O$ emission from agricultural soils.

## 5.3 References


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# APPENDICES

## Supplementary Material for Chapter 3

### Nitrous oxide fluxes from liquid pig manure and urea fertilizer applied field

**Table S1.** Chemical composition and rate of nitrogen in the liquid pig manure (LPM) and urea fertilizer (FER) applied to the plot in 2012.

| Manure Composition | | | | N Application rates | | | |
|---|---|---|---|---|---|---|---|
| **Year** | **Dry matter** | **Total N** | **$NH_4^+$-N** | **Volume of LPM** | **Total Manure N applied** | **LPM Total Available N applied** | **FER Urea N applied** |
| | (kg $kg^{-1}$) | (mg $L^{-1}$) | (mg $L^{-1}$) | (L $ha^{-1}$) | (kg N $ha^{-1}$) | (kg N $ha^{-1}$) | (kg N ha-1) |
| 2012 | 0.092 | 5935 | 3047 | 56,000 | 330 | 210 | 83 |

Note: Total available N applied is the amount of N expected to be available in soil for plant use within a year, this is calculated as

$$\begin{aligned} &\mathit{Total\ Available\ N} \\ &= \mathrm{NH_4^+\text{-}N} \times (100 - 25\,\%\ \mathrm{NH_4^+}\text{-}N\ \mathit{volatilization\ loss}) + 25\,\%\ \mathit{Organic\ N} \end{aligned}$$

**Table S2** Total precipitation, monthly mean air temperature and record daily high temperature on the study site compared with the 30-year average for the region, Carberry, Manitoba, Canada for the period 2012 (Environment Canada 2014).

| | **Total Precipitation** | | **Mean Temperature** | | **Record Daily High Temperature** | |
|---|---|---|---|---|---|---|
| **Month** | **2012 †** | **30 yr** | **2012** | **30 yr** | **2012** | **30 yr** |
| | ------------- (mm) ------------- | | ------------- (°C) ---------------- | | -------- (°C) --------- | |
| January | 7.0 | 20.0 | -11.0 | -19.2 | 8.2 | 5.2 |
| February | 3.1 | 34.0 | -8.5 | -10.4 | 7.1 | 7.7 |
| March | 31.3 | 30.0 | 1.6 | -6.8 | 23.7 | 16.3 |
| April | 32.6 | 19.0 | 5.9 | 3.2 | 24.3 | 27.8 |
| May | 128.0 | 70.0 | 11.2 | 9.9 | 30.5 | 31 |
| June | 79.7 | 84.0 | 17.4 | 15 | 30.7 | 34.7 |
| July | 138.5 | 77.0 | 21.2 | 17.8 | 34.7 | 31.8 |
| August | 68.8 | 64.0 | 18.5 | 17.9 | 36.8 | 34 |
| September | 7.3 | 53.0 | 12.2 | 11.8 | 30.2 | 33.4 |
| October | 59.1 | 32.0 | 3.3 | 4.8 | 20.7 | 28.6 |
| November | 25.2 | 25.0 | -8.3 | -6.0 | 5.5 | 19.3 |
| December | 7.7 | 22.0 | -15.7 | -13.8 | 3.6 | 7.5 |
| **Total** | **588.3** | **530.0** | | | | |
| **Average** | | | **4.0** | **2.0** | | |
| **Maximum** | | | | | **36.8** | **34.7** |

† M indicate missing values from weathers station.

**Table S3** Cumulative nitrous oxide flux, emission factor emission intensity and grain yield from the control (CON), liquid pig manure (LPM) and urea fertilizer (FER) treatment plots during each growing season of the study.

| **Year (crop)** | **Treatment** | **Cumulative $N_2O$ †** | **Soil nitrate** | **Soil ammonium** | **Grain yield †** | **Plant N Uptake** | **Emission intensity †** | **$N_2O$ emission factor Total N †** | **$N_2O$ emission factor Total Available N †** |
|---|---|---|---|---|---|---|---|---|---|
| | | (kg N $ha^{-1}$) | mg N $kg^{-1}$ | mg N $kg^{-1}$ | (Mg $ha^{-1}$) | (kg N $ha^{-1}$) | (kg $N_2O$-N $Mg^{-1}$ of yield) | (% kg N $kg^{-1}$ N) | (% kg N $kg^{-1}$ N) |
| **2012** | CON | 0.32*b* | 14.62*c* | 1.84*b* | 1.718*a* | 63*a* | 0.22*b* | | |
| (Wheat) | FER | 1.09*b* | 29.64*b* | 5.41a*b* | 2.005*a* | 84*a* | 0.56*b* | 0.93a | 0.93a |
| | LPM | 27.30*a* | 71.19*a* | 16.17*a* | 2.515*a* | 106*a* | 10.70*a* | 8.18a | 12.84a |

† LS-means with the same letter within a column for a given year are not significantly different (Tukey-Kramer groupings, alpha=0.05).

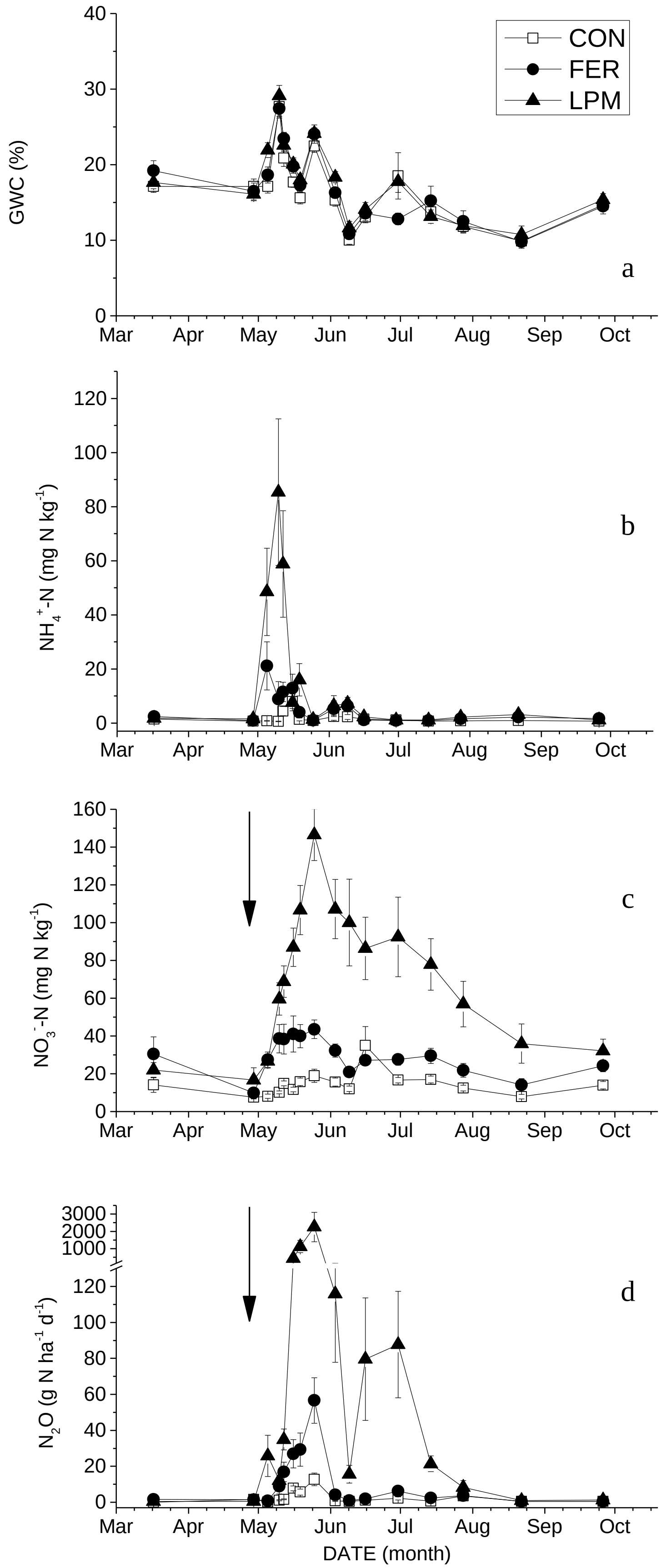


Fig. S1. Gravimetric soil moisture (0-10 cm soil depth) (a), soil ammonium (b), soil nitrate (c), and nitrous oxide flux (d) from liquid pig manure (LPM), urea fertilizer (FER) and control (CON) treatments in 2012. Values are means (n = 12) ± SE. Arrow indicate time of N application on 16th May 2012.